

06/21/94

Project unit: CHEM ENGR Unit code: 02.010.114  
Project director(s): WINNICK J CHEM ENGR (404)894-2839

Title: HIGH-TEMPERATURE MEMBRANES FOR H<sub>2</sub>S AND SO<sub>2</sub> SEPARATIONS

AMENDMENT # M006 PROVIDES A NO-COST EXTENSION TO SEPTEMBER 30, 1994.

GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 01/27/95

Project No. E-19-669\_\_\_\_\_ Center No. 10/24-6-R7037-0A0\_

Project Director WINNICK J\_\_\_\_\_ School/Lab CHEM ENGR\_\_\_\_\_

Sponsor US DEPT OF ENERGY/DOE PITTSBURGH - PA\_\_\_\_\_

Contract/Grant No. DE-FG22-90PC90293\_\_\_\_\_ Contract Entity GTRC

Prime Contract No. \_\_\_\_\_

Title HIGH-TEMPERATURE MEMBRANES FOR H2S AND SO2 SEPARATIONS\_\_\_\_\_

Effective Completion Date 940930 (Performance) 941230 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	Y	_____
Government Property Inventory & Related Certificate	Y	941129
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments\_\_\_\_\_

Subproject Under Main Project No. \_\_\_\_\_

Continues Project No. \_\_\_\_\_

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

NOTE: Final Patent Questionnaire sent to PDPI.

**Georgia Institute of Technology**  
Lyman Hall/Emerson Building  
Atlanta, Georgia 30332-0259  
404-894-4624; 2629

October 11, 1991

Ms. Rhonda Dupree, Contract Specialist  
AD-22, MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Dupree,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period July 1, 1991 through September 30, 1991. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/GMR/djt

Enclosure

cc: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Mary Wolfe, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b>  0348-0039	<b>Page</b>  1	<b>of</b>  1 pages
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384						
<b>4. Employer Identification Number</b>  58-0603146		<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-0A0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) August 31, 1983		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) July 01, 1991		To: (Month, Day, Year) September 30, 1991
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative
a. Total outlays				53,124.11	22,991.90	76,116.01
b. Recipient share of outlays				-0-	-0-	-0-
c. Federal share of outlays				53,124.11	22,991.90	76,116.01
d. Total unliquidated obligations						30,893.59
e. Recipient share of unliquidated obligations						-0-
f. Federal share of unliquidated obligations						30,893.59
g. Total Federal share (Sum of lines c and f)						107,009.60
h. Total Federal funds authorized for this funding period						199,613.00
i. Unobligated balance of Federal funds (Line h minus line g)						92,603.40
<b>11. Indirect Expense</b>						
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input checked="" type="checkbox"/> Fixed						
b. Rate SEE BELOW		c. Base MTDC		d. Total Amount - 0 -		e. Federal Share - 0 -
<b>12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b>  <div style="text-align: right;">                         Questions pertaining to this report should be directed to: Ms. Geraldine Reese                          (404) 894-2629                     </div> GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30						
<b>13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.</b>						
Typed or Printed Name and Title  David V. Welch, Director, Grants and Contracts Accounting					Telephone (Area code, number and extension)  (404) 894-2629	
Signature of Authorized Certifying Official  					Date Report Submitted  October 11, 1991	

NSN 7540-01-218-4387

Direct Costs

269-201

Indirect Costs

FY91 @ 62.5% - Fixed

32,691.76

20,432.35

FY92 @ 61.5% - Provisional

14,236.47

8,755.43

Standard Form 269A (REV 4-88)  
Prescribed by OMB Circulars A-102 and A-110



# FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 80-RO182  
1. Federal sponsoring agency and organizational element to which this report is submitted

U. S. DEPARTMENT OF ENERGY

## 2. RECIPIENT ORGANIZATION

Name : GEORGIA TECH RESEARCH CORPORATION

Number and Street : P. O. BOX 100117

City, State and ZIP Code: ATLANTA, GA 30384

3. FEDERAL EMPLOYER IDENTIFICATION NO. 58-0603146

4. Federal grant or other identification number  
DE-FG22-90PC90293  
5. Recipient's account number or identifying number  
E-19-669/R7037-OAO  
6. Letter of credit number  
7. Last payment voucher number

Give total number for this period

8. Payment Vouchers credited to your account  
9. Treasury checks received (whether or not deposited)

## 10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year) TO (month, day year)  
July 01, 1991 September 30, 1991

## 11. STATUS OF

FEDERAL

CASH

(See specific instructions on the back)

a. Cash on hand beginning of reporting period	\$ (19,265.80)
b. Letter of credit withdrawals	-0-
c. Treasury check payments	8,904.98
d. Total receipts (Sum of lines b and c)	8,904.98
e. Total cash available (Sum of lines a and d)	(10,360.82)
f. Gross disbursements	22,991.90
g. Federal share of program income	-0-
h. Net disbursements (Line f minus line g)	22,991.90
i. Adjustments of prior periods	-0-
j. Cash on hand end of period	\$ (33,352.72)

12. THE AMOUNT SHOWN ON LINE 11J, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING

Days

## 13. OTHER INFORMATION

a. Interest income	\$
b. Advances to subgrantees or subcontractors	\$

14. REMARKS (Attach additional sheets of plain paper, if more space is required)

Questions pertaining to this report should be directed to: Ms. Geraldine Reese (404) 894-2629

## 15. CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement

AUTHORIZED  
CERTIFYING  
OFFICIAL

SIGNATURE

TYPED OR PRINTED NAME AND TITLE

David V. Welch, Director  
Grants and Contracts Accounting

DATE REPORT SUBMITTED

October 11, 1991

TELEPHONE (Area Code, Number, Extension)

(404) 894-2629

THIS SPACE FOR AGENCY USE



Office of Grants and Contracts Accounting

**Georgia Institute of Technology**  
Hinman Building  
Atlanta, Georgia 30332-0259  
404-894-4624; 2629  
Fax: 404-894-5519

July 28, 1992

Ms. Rhonda Dupree, Contract Specialist  
AD-22, MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

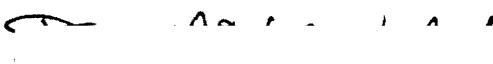
REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Dupree,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period April 01, 1992 through June 30, 1992. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contract Geraldine Reese of this office at (404) 894-2629.

Sincerely,

  
David V. Welch  
Director

DVW/GMR/djt

Enclosure

c: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Mary Wolfe, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b> 0348-0039		<b>Page</b> 1		<b>of</b> 1 pages	
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384									
<b>4. Employer Identification Number</b>  58-0603146			<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-0A0			<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual	
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990				To: (Month, Day, Year) August 31, 1993		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) April 01, 1992		To: (Month, Day, Year) June 30, 1992	
<b>10. Transactions:</b>				I Previously Reported		II This Period		III Cumulative	
a. Total outlays				102,375.39		8,419.01		110,794.40	
b. Recipient share of outlays				-0-		-0-		-0-	
c. Federal share of outlays				102,375.39		8,419.01		110,794.40	
d. Total unliquidated obligations								86.93	
e. Recipient share of unliquidated obligations								-0-	
f. Federal share of unliquidated obligations								86.93	
g. Total Federal share (Sum of lines c and f)								110,881.33	
h. Total Federal funds authorized for this funding period								199,613.00	
i. Unobligated balance of Federal funds (Line h minus line g)								88,731.67	
<b>11. Indirect Expense</b>		<b>a. Type of Rate (Place "X" in appropriate box)</b> <input type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input checked="" type="checkbox"/> Fixed							
<b>b. Rate</b> SEE ATTACHED		<b>c. Base</b> MTDC		<b>d. Total Amount</b> 3,206.00		<b>e. Federal Share</b> 3,206.00			
<b>12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b> <p style="text-align: center;">Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629</p> GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30									
<b>13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.</b>									
<b>Typed or Printed Name and Title</b>  David V. Welch, Director, Grants & Contracts Acctg.						<b>Telephone (Area code, number and extension)</b>  (404) 894-2629			
<b>Signature of Authorized Certifying Official</b>						<b>Date Report Submitted</b>  July 28, 1992			

E-19-669/R7037-0A0  
FINANCIAL STATUS REPORT  
GRANT NO. DE-FG22-90PC90293  
Period Covering: 04/01/92 - 06/30/92

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @62.5% Fixed	32,691.76	20,432.35
FY92 @61.5% Fixed	35,709.16	21,961.13

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
04/01/92 - 06/30/92	5,213.01	3,206.00

**Georgia Institute of Technology**

Hinman Building  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

January 20, 1993

Ms. Rhonda Dupree, Contract Specialist  
AD-22, MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Dupree,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period October 01, 1992 through December 31, 1992. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/GMR/djt

Enclosure

cc: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Mary Wolfe, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b>  0348-0039		<b>Page</b>  1		<b>of</b>  2 pages	
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 10C117 ATLANTA, GA 30384									
<b>4. Employer Identification Number</b>  58-0603146			<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-OAO			<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual	
<b>8. Funding/Grant Period (See instructions)</b> From: (Month, Day, Year) September 01, 1990			To: (Month, Day, Year) August 31, 1993			<b>9. Period Covered by this Report</b> From: (Month, Day, Year) October 01, 1992		To: (Month, Day, Year) December 31, 1992	
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative			
a. Total outlays				139,111.17	5,649.73	144,760.90			
b. Recipient share of outlays				-0-	-0-	-0-			
c. Federal share of outlays				139,111.17	5,649.73	144,760.90			
d. Total unliquidated obligations						11,298.27			
e. Recipient share of unliquidated obligations						-0-			
f. Federal share of unliquidated obligations						11,298.27			
g. Total Federal share (Sum of lines c and f)						156,059.17			
h. Total Federal funds authorized for this funding period						199,613.00			
i. Unobligated balance of Federal funds (Line h minus line g)						43,553.83			
<b>11. Indirect Expense</b>									
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed									
b. Rate SEE ATTACHED			c. Base MTDC		d. Total Amount 2,009.44		e. Federal Share 2,009.44		
<b>12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b>  <div style="text-align: right; padding-right: 50px;">                         Questions pertaining to this report should be directed to: Ms. Geraldine Reese (404) 894-2629                     </div> GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30									
<b>13. Certification:</b> I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.									
Typed or Printed Name and Title  David V. Welch, Director, Grants and Contracts Accounting						Telephone (Area code, number and extension)  (404) 894-2629			
Signature of Authorized Certifying Official  						Date Report Submitted  January 20, 1993			

January 20, 1993  
Financial Status Report (Attachment)  
Grant No. DE-FG22-90PC90293  
Period Covering: 10/01/92 - 12/31/92

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @62.5% Fixed	32,691.76	20,432.35
FY92 @61.5% Fixed	35,709.16	21,961.13
FY93 @55.2% Provisional	21,885.63	12,080.87

	<u>REPORT PERIOD</u>	
	<u>Direct Costs</u>	<u>Indirect Costs</u>
10/01/92 - 12/31/92	3,640.29	2,009.44

Georgia Institute of Technology  
Hinman Building  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

April 19, 1993

Ms. Rhonda Dupree, Contract Specialist  
AD-22, MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Dupree,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period January 01, 1993 through March 31, 1993. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

20

David V. Welch  
Director

DVW/GMR/djt

Enclosures

cc: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Danielle Herrmann, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

RECEIVED

APR 22 1993

OFFICE OF CONTRACT  
ADMINISTRATION



# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b> 0348-0039		<b>Page of</b> 1 2 pages	
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384							
<b>4. Employer Identification Number</b>  58-0603146		<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-OA0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual	
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) August 31, 1993		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) January 01, 1993		To: (Month, Day, Year) March 31, 1993	
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative	
a. Total outlays				144,760.90	6,070.79	150,831.69	
b. Recipient share of outlays				-0-	-0-	-0-	
c. Federal share of outlays				144,760.90	6,070.69	150,831.69	
d. Total unliquidated obligations						5,690.91	
e. Recipient share of unliquidated obligations						-0-	
f. Federal share of unliquidated obligations						5,690.91	
g. Total Federal share (Sum of lines c and f)						156,522.60	
h. Total Federal funds authorized for this funding period						199,613.00	
i. Unobligated balance of Federal funds (Line h minus line g)						43,090.40	
<b>11. Indirect Expense</b>							
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed							
b. Rate SEE ATTACHED		c. Base MTDC		d. Total Amount \$2,159.20		e. Federal Share \$2,159.20	
<b>12. Remarks:</b> Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.  Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629							
GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30							
<b>13. Certification:</b> I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.							
Typed or Printed Name and Title  David V. Welch, Director, Grants and Contracts Accounting					Telephone (Area code, number and extension)  (404) 894-2629		
Signature of Authorized Certifying Official					Date Report Submitted  April 19, 1993		

April 19, 1993

Financial Status Report (Attachment) Page 2 of 2  
Grant No. DE-FG22-90PC90293  
Period Covering: 01/01/93 - 03/31/93

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Fixed	35,709.16	21,961.13
FY93 @ 55.2% Provisional	25,797.22	14,240.07

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
01/01/93 - 03/31/93	3,911.59	2,159.20

RECEIVED

AUG 11 1993

OFFICE OF CONTRACT  
ADMINISTRATION

August 5, 1993

Georgia Institute of Technology

190 Bobby Dodd Way

Atlanta, Georgia 30332-0259

USA

404•894•4624; 2629

Fax: 404•894•5519

Ms. Nancy Toppetta  
MS 921-118  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
Acquisition and Assistance Division  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Toppetta,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period April 01, 1993 through June 30, 1993. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/GMR/djt

Enclosures

c: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Wanda Simon, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

Federal Agency and Organizational Element to Which Report is Submitted U. S. DEPARTMENT OF ENERGY	2 Federal Grant or Other Identifying Number Assigned By Federal Agency DE-FG22-90PC90293	OMB Approval No. 0348-0039	Page 1	of 2 pages
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Recipient Organization (Name and complete address, including ZIP code) GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384
--

Employer Identification Number 58-0603146	5. Recipient Account Number or Identifying Number E-19-669/R7037-OAO	6. Final Report <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	7. Basis <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual
--	---	--	---

Funding/Grant Period (See Instructions) From: (Month, Day, Year) September 01, 1990	To: (Month, Day, Year) August 31, 1993	9. Period Covered by this Report From: (Month, Day, Year) April 01, 1993	To: (Month, Day, Year) June 30, 1993
---	---	--	---

D. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	150,831.69	5,808.24	156,639.93
b. Recipient share of outlays	-0-	-0-	-0-
c. Federal share of outlays	150,831.69	5,808.24	156,639.93
d. Total unliquidated obligations			504.33
e. Recipient share of unliquidated obligations			-0-
f. Federal share of unliquidated obligations			504.33
g. Total Federal share (Sum of lines c and f)			157,144.26
h. Total Federal funds authorized for this funding period			199,613.00
i. Unobligated balance of Federal funds (Line h minus line g)			42,468.74

Indirect Expense	a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input checked="" type="checkbox"/> Fixed			
	b. Rate SEE ATTACHED	c. Base MTDC	d. Total Amount 2,065.82	e. Federal Share 2,065.82

Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30

Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.

Signed or Printed Name and Title David V. Welch, Director, Grants and Contracts Accounting	Telephone (Area code, number and extension) (404) 894-2629
Signature of Authorized Certifying Official 	Date Report Submitted August 5, 1993

Financial Status Report (08/05/93)  
U. S. Department of Energy  
Grant No. DE-FG22-90PC90293 (E-19-669/R7037-OA0)  
Period Covering: 04/01/93 - 06/30/93

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Fixed	35,709.16	21,961.13
FY93 @ 55.2% Provisional	29,539.64	16,305.89

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
04/01/93 - 06/30/93	3,742.42	2,065.82

Georgia Institute of Technology  
190 Bobby Dodd Way  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

October 20, 1993

Ms. Nancy Toppetta, Contract Specialist  
MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Toppetta,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period July 01, 1993 through September 30, 1993. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/GMR/djt

Enclosures

cc: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Wanda Simon, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

RECEIVED

OCT 27 1993

OFFICE OF CONTRACT  
ADMINISTRATION

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b> 0348-0039	<b>Page</b> 1	<b>of</b> 2 pages
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384						
<b>4. Employer Identification Number</b>  58-0603146		<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-OA0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) December 31, 1993		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) July 01, 1993		To: (Month, Day, Year) September 30, 1993
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative
a. Total outlays				156,639.93	19,589.71	176,229.64
b. Recipient share of outlays				-0-	-0-	-0-
c. Federal share of outlays				156,639.93	19,589.71	176,229.64
d. Total unliquidated obligations						73.76
e. Recipient share of unliquidated obligations						-0-
f. Federal share of unliquidated obligations						73.76
g. Total Federal share (Sum of lines c and f)						176,303.40
h. Total Federal funds authorized for this funding period						199,613.00
i. Unobligated balance of Federal funds (Line h minus line g)						23,309.60
<b>11. Indirect Expense</b>						
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed						
b. Rate SEE ATTACHED		c. Base MTDC		d. Total Amount 5,290.65		e. Federal Share 5,290.65
<b>12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b>  <div style="text-align: right;">           Questions pertaining to this report should            be directed to: Geraldine Reese            (404) 894-2629         </div>						
GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30						
<b>13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.</b>						
<b>Typed or Printed Name and Title</b>  David V. Welch, Director, Grants and Contracts Accounting					<b>Telephone (Area code, number and extension)</b>  (404) 894-2629	
<b>Signature of Authorized Certifying Official</b>  					<b>Date Report Submitted</b>  October 20, 1993	

Financial Status Report  
U. S. Department of Energy  
Grant No. DE-FG22-90PC90293  
Period Covering: 07/01/93 - 09/30/93

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Provisional	35,709.16	21,961.13
FY93 @ 55.2% Provisional	29,539.64	16,305.89
FY94 @ 37.0% Provisional	14,299.06	5,290.65

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
07/01/93 - 09/30/93	14,299.06	5,290.65



# FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 80-RO182

1. Federal sponsoring agency and organizational element to which this report is submitted

U. S. DEPARTMENT OF ENERGY

## 2. RECIPIENT ORGANIZATION

Name : GEORGIA TECH RESEARCH CORPORATION

Number and Street : P. O. BOX 100117

City, State and ZIP Code : ATLANTA, GA 30384

4. Federal grant or other identification number  
DE-FG22-90PC90293

5. Recipient's account number or identifying number  
E-19-669/R7037-OA0

6. Letter of credit number

7. Last payment voucher number

Give total number for this period

8. Payment Vouchers credited to your account

9. Treasury checks received (whether or not deposited)

## 10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year)

July 01, 1993

TO (month, day year)

September 30, 1993

## 3. FEDERAL EMPLOYER IDENTIFICATION NO.

58-0603146

## 11. STATUS OF

FEDERAL

CASH

(See specific instructions on the back)

a. Cash on hand beginning of reporting period

\$ (10,201.62)

b. Letter of credit withdrawals

-0-

c. Treasury check payments

8,122.87

d. Total receipts (Sum of lines b and c)

8,122.87

e. Total cash available (Sum of lines a and d)

(2,078.75)

f. Gross disbursements

19,589.71

g. Federal share of program income

-0-

h. Net disbursements (Line f minus line g)

19,589.71

i. Adjustments of prior periods

-0-

j. Cash on hand end of period

\$ (21,668.46)

12. THE AMOUNT SHOWN ON LINE 11j, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING

Days

## 13. OTHER INFORMATION

a. Interest income

\$

b. Advances to subgrantees or subcontractors

\$

## 14. REMARKS (Attach additional sheets of plain paper, if more space is required)

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

## 15.

### CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement

AUTHORIZED  
CERTIFYING  
OFFICIAL

SIGNATURE

TYPED OR PRINTED NAME AND TITLE

David V. Welch, Director  
Grants and Contracts Accounting

DATE REPORT SUBMITTED

October 20, 1993

TELEPHONE (Area Code, Number, Extension)

(404) 894-2629

THIS SPACE FOR AGENCY USE

Georgia Institute of Technology  
190 Bobby Dodd Way  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

January 18, 1994

Ms. Nancy Toppetta, Contract Specialist  
MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Toppetta,

Enclosed is the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period October 01, 1993 through December 31, 1993. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/GMR/djt

Enclosures

c: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01, MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Wanda Simon, OCA/CSD 0420 (SF-269A) ✓  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b>  0348-0039	<b>Page</b>  1	<b>of</b>  2 pages
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384						
<b>4. Employer Identification Number</b>  58-0603146		<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-0A0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) June 30, 1994		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) October 01, 1993		To: (Month, Day, Year) December 31, 1993
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative
a. Total outlays				176,229.64	18,120.06	194,349.70
b. Recipient share of outlays				-0-	-0-	-0-
c. Federal share of outlays				176,229.64	18,120.06	194,349.70
d. Total unliquidated obligations						2,564.93
e. Recipient share of unliquidated obligations						-0-
f. Federal share of unliquidated obligations						2,564.93
g. Total Federal share (Sum of lines c and f)						196,914.63
h. Total Federal funds authorized for this funding period						199,613.00
i. Unobligated balance of Federal funds (Line h minus line g)						2,698.37
<b>11. Indirect Expense</b>						
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed						
b. Rate SEE ATTACHED		c. Base MTDC		d. Total Amount 4,893.74		e. Federal Share 4,893.74
<b>12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b>  <div style="text-align: right;">                         Questions pertaining to this report should                          be directed to: Geraldine Reese                          (404) 894-2629                     </div> GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30						
<b>13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.</b>						
Typed or Printed Name and Title  David V. Welch, Director, Grants & Contracts Accounting					Telephone (Area code, number and extension)  (404) 894-2629	
Signature of Authorized Certifying Official  					Date Report Submitted  January 18, 1994	

FINANCIAL STATUS REPORT  
U. S. DEPARTMENT OF ENERGY  
GRANT NO. DE-FG22-90PC90293 (E-19-669/R7037-0A0)  
PERIOD COVERING: 10/01/93 - 12/31/93

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Provisional	35,709.16	21,961.13
FY93 @ 55.2% Provisional	29,539.64	16,305.89
FY94 @ 37.0% Provisional	27,525.38	10,184.39

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
10/01/93 - 12/31/93	13,226.32	4,893.74

# FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 83-RO187

1. Federal sponsoring agency and organizational element to which this report is submitted

U. S. DEPARTMENT OF ENERGY

## 2. RECIPIENT ORGANIZATION

Name : GEORGIA TECH RESEARCH CORPORATION

Number and Street : P. O. BOX 100117

ATLANTA, GA 30384

City, State and ZIP Code:

4. Federal grant or other identification number  
DE-FG22-90PC90293

5. Recipient's account number or identifying number

E-19-669/R7037-OAO

6. Letter of credit number

7. Last payment voucher number

Give total number for this period

8. Payment Vouchers credited to your account

9. Treasury checks received (whether or not deposited)

## 10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year)  
October 01, 1993

TO (month, day, year)  
December 31, 1993

## 3. FEDERAL EMPLOYER IDENTIFICATION NO.

58-0603146

## 11. STATUS OF

FEDERAL

CASH

(See specific instructions on the back)

a. Cash on hand beginning of reporting period

\$ (21,668.46)

b. Letter of credit withdrawals

-0-

c. Treasury check payments

21,668.46

d. Total receipts (Sum of lines b and c)

21,668.46

e. Total cash available (Sum of lines a and d)

-0-

f. Gross disbursements

18,120.06

g. Federal share of program income

-0-

h. Net disbursements (Line f minus line g)

18,120.06

i. Adjustments of prior periods

-0-

j. Cash on hand end of period

\$ (18,120.06)

12. THE AMOUNT SHOWN ON LINE 11J, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING

Days

## 13. OTHER INFORMATION

a. Interest income

\$

b. Advances to subgrantees or subcontractors

\$

## 14. REMARKS (Attach additional sheets of plain paper, if more space is required)

Questions pertaining to this report should be directed to: Geraldine Reese (404) 894-2629

## 15. CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement

AUTHORIZED

CERTIFYING

OFFICIAL

SIGNATURE



TYPED OR PRINTED NAME AND TITLE

David V. Welch, Director  
Grants & Contracts Accounting

DATE REPORT SUBMITTED

January 18, 1994

TELEPHONE (Area Code, Number, Extension)

(404) 894-2629

THIS SPACE FOR AGENCY USE

**Georgia Institute of Technology**

190 Bobby Dodd Way  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

April 25, 1994

Ms. Nancy Toppetta, Contract Specialist  
MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Toppetta,

Enclosed are the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period January 01, 1994 through March 31, 1994. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (494) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/djt

Enclosures

c: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01-MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 9210232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Wanda Simon, OCA/CSD 0420 (SF-269A)  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b> 0348-0039	<b>Page</b> 1	<b>of</b> 2 pages	
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384							
<b>4. Employer Identification Number</b>  58-0603146	<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-0A0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual		
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) June 30, 1994		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) January 01, 1994		To: (Month, Day, Year) March 31, 1994	
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative	
a. Total outlays				194,349.70	2,716.59	197,066.29	
b. Recipient share of outlays				-0-	-0-	-0-	
c. Federal share of outlays				194,349.70	2,716.59	197,066.29	
d. Total unliquidated obligations						2,064.60	
e. Recipient share of unliquidated obligations						-0-	
f. Federal share of unliquidated obligations						2,064.60	
g. Total Federal share (Sum of lines c and f)						199,130.89	
h. Total Federal funds authorized for this funding period						199,613.00	
i. Unobligated balance of Federal funds (Line h minus line g)						482.11	
<b>1. Indirect Expense</b>							
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed							
b. Rate SEE ATTACHED		c. Base MTDC		d. Total Amount \$733.68		e. Federal Share \$733.68	
<b>2. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b>  <p style="text-align: center;">Questions concerning this report should be directed to:                  Geraldine Reese (404) 894-2629</p> GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30							
<b>3. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.</b>							
Typed or Printed Name and Title  David V. Welch, Director, Grants & Contracts Accounting					Telephone (Area code, number and extension)  (404) 894-2629		
Signature of Authorized Certifying Official  					Date Report Submitted  April 25, 1994		

Attachment

PAGE 2 OF 2

Financial Status Report (04/25/94)

U. S. Department of Energy

Grant No. DE-FG22-90PC90293 (E-19-669/R7037-0A0)

Period Covering: 01/01/94 - 03/31/94

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Provisional	35,709.16	21,961.13
FY93 @ 55.2% Provisional	29,539.64	16,305.89
FY94 @ 37.0% Provisional	29,508.29	10,918.07

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
01/01/94 - 03/31/94	1,982.91	733.68



**Georgia Institute of Technology**

190 Bobby Dodd Way  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

August 5, 1994

Ms. Nancy Toppetta, Contract Specialist  
MS 921-165  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Ms. Toppetta,

Enclosed are the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period April 01, 1994 through June 30, 1994. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (494) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/djt

Enclosures

c: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01-MS 922-206  
Mr. William Maro (w/copy SF-269A & SF-272)  
AD-30, MS 9210232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Wanda Simon, OCA/CSD 0420 (SF-269A)  
File: E-19-669/R7037-0A0

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b> <b>0348-0039</b>		<b>Page</b> 1 <b>of</b> 2 <b>pages</b>																	
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> GEORGIA TECH RESEARCH CORPORATION P. O. BOX 100117 ATLANTA, GA 30384																							
<b>4. Employer Identification Number</b>  58-0603146		<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-0A0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual																	
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) September 30, 1994		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) April 01, 1994		To: (Month, Day, Year) June 30, 1994																	
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative																	
a. Total outlays				197,066.29	1,732.21	198,798.50																	
b. Recipient share of outlays				-0-	-0-	-0-																	
c. Federal share of outlays				197,066.29	1,732.21	198,798.50																	
d. Total unliquidated obligations						814.50																	
e. Recipient share of unliquidated obligations						-0-																	
f. Federal share of unliquidated obligations						814.50																	
g. Total Federal share (Sum of lines c and f)						199,613.00																	
h. Total Federal funds authorized for this funding period						199,613.00																	
i. Unobligated balance of Federal funds (Line h minus line g)						-0-																	
<b>11. Indirect Expense</b> <table style="width: 100%; border: none;"> <tr> <td colspan="8">           a. Type of Rate (Place "X" in appropriate box)  <input checked="" type="checkbox"/> Provisional      <input checked="" type="checkbox"/> Predetermined      <input type="checkbox"/> Final      <input type="checkbox"/> Fixed         </td> </tr> <tr> <td colspan="2">b. Rate SEE ATTACHED</td> <td colspan="2">c. Base MTDC</td> <td colspan="2">d. Total Amount 467.82</td> <td colspan="2">e. Federal Share 467.82</td> </tr> </table>								a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input checked="" type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed								b. Rate SEE ATTACHED		c. Base MTDC		d. Total Amount 467.82		e. Federal Share 467.82	
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input checked="" type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed																							
b. Rate SEE ATTACHED		c. Base MTDC		d. Total Amount 467.82		e. Federal Share 467.82																	
<b>12. Remarks:</b> Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.  Questions concerning this report should be directed to: Geraldine Reese (404) 894-2629  GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30																							
<b>13. Certification:</b> I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.																							
Typed or Printed Name and Title  David V. Welch, Director, Grants and Contracts Accounting						Telephone (Area code, number and extension)  (404) 894-2629																	
Signature of Authorized Certifying Official						Date Report Submitted  August 5, 1994																	

Attachment

Page 2 of 2

Financial Status Report (08/05/94)

U. S. Department of Energy

Grant No. DE-FG22-90PC90293 (E-19-669/R7037-0A0)

Period Covering: 04/01/94 - 06/30/94

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Provisional	35,709.16	21,961.13
FY93 @ 55.2% Provisional	29,539.64	16,305.89
FY94 @ 37.0% Provisional	30,772.68	11,385.89

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
04/01/94 - 06/30/94	1,264.39	467.82

**Georgia Institute of Technology**  
190 Bobby Dodd Way  
Atlanta, Georgia 30332-0259  
USA  
404•894•4624; 2629  
Fax: 404•894•5519

January 23, 1995

Mr. Andrew Ferlic  
MS 921-118  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, PA 15236-0940

REFERENCE: Grant No. DE-FG22-90PC90293

Dear Mr. Ferlic,

Enclosed are the Financial Status Report (SF-269A) and the Federal Cash Transactions Report (SF-272) covering the period July 01, 1994 through September 30, 1994. The reports are being distributed in accordance with the Federal Assistance Report checklist.

If you should have questions or need additional information, please contact Geraldine Reese of this office at (404) 894-2629.

Sincerely,

David V. Welch  
Director

DVW/djt

Enclosures

c: Ms. Marilyn Keane (w/copy SF-269A)  
PM-01-MS 922-206  
Mr. William Maro (w/copy SF-269A)  
AD-30, MS 921-232  
Dr. Jack Winnick, Chemical Eng, 0100 (SF-269A)  
Ms. Wanda Simon, OCA/CSD 0420 (SF-269A)  
File: E-19-669/R7037-0A0

# FEDERAL CASH TRANSACTIONS REPORT

(See instructions on the back. If report is for more than one grant or assistance agreement, attach completed Standard Form 272-A.)

Approved by Office of Management and Budget, No. 80-RO182

1. Federal sponsoring agency and organizational element to which this report is submitted

U. S. DEPARTMENT OF ENERGY

## 2. RECIPIENT ORGANIZATION

Name : GEORGIA TECH RESEARCH CORPORATION

Number and Street : 400 10TH STREET, N.W. - ROOM 270

City, State and ZIP Code: ATLANTA, GA 30332-0415

4. Federal grant or other identification number  
DE-FG22-90PC90293

5. Recipient's account number or identifying number  
E-19-669/R7037-0A0

6. Letter of credit number

7. Last payment voucher number

Give total number for this period

8. Payment Vouchers credited to your account

9. Treasury checks received (whether or not deposited)

## 10. PERIOD COVERED BY THIS REPORT

FROM (month, day, year)  
July 01, 1994

TO (month, day, year)  
September 30, 1994

## 3. FEDERAL EMPLOYER IDENTIFICATION NO.

58-0603146

## 11. STATUS OF

FEDERAL

CASH

(See specific instructions on the back)

a. Cash on hand beginning of reporting period

\$ (1,181.63)

b. Letter of credit withdrawals

-0-

c. Treasury check payments

-0-

d. Total receipts (Sum of lines b and c)

-0-

e. Total cash available (Sum of lines a and d)

(1,181.63)

f. Gross disbursements

637.52

g. Federal share of program income

-0-

h. Net disbursements (Line f minus line g)

637.52

i. Adjustments of prior periods

-0-

j. Cash on hand end of period Includes \$1,165.85 retained by DOE #37 \$1,097.35

\$ (1,819.15)

## 12. THE AMOUNT SHOWN ON LINE 11j, ABOVE, REPRESENTS CASH REQUIREMENTS FOR THE ENSUING

Days

## 13. OTHER INFORMATION #38 68.50

a. Interest income

\$1,165.85

\$

b. Advances to subgrantees or subcontractors

\$

## 14. REMARKS (Attach additional sheets of plain paper, if more space is required)

Questions concerning this report should be directed to:  
Geraldine Reese (404) 894-2629

## 15.

## CERTIFICATION

I certify to the best of my knowledge and belief that this report is true in all respects and that all disbursements have been made for the purpose and conditions of the grant or agreement

AUTHORIZED  
CERTIFYING  
OFFICIAL

SIGNATURE

TYPED OR PRINTED NAME AND TITLE

David V. Welch, Director  
Grants and Contracts Accounting

DATE REPORT SUBMITTED

January 23, 1995

TELEPHONE (Area Code, Number, Extension)

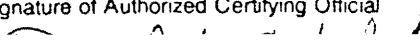
(404) 894-2629

THIS SPACE FOR AGENCY USE

# FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

<b>1. Federal Agency and Organizational Element to Which Report is Submitted</b>  U. S. DEPARTMENT OF ENERGY		<b>2. Federal Grant or Other Identifying Number Assigned By Federal Agency</b>  DE-FG22-90PC90293		<b>OMB Approval No.</b>  0348-0039	<b>Page</b>  1	<b>of</b>  2 pages
<b>3. Recipient Organization (Name and complete address, including ZIP code)</b> Georgia Tech Research Corporation 400 10th Street, N.W. - Room 270 Atlanta, GA 30332-0415						
<b>4. Employer Identification Number</b>  58-0603146		<b>5. Recipient Account Number or Identifying Number</b>  E-19-669/R7037-0A0		<b>6. Final Report</b> <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		<b>7. Basis</b> <input checked="" type="checkbox"/> Cash <input type="checkbox"/> Accrual
<b>8. Funding/Grant Period (See Instructions)</b> From: (Month, Day, Year) September 01, 1990		To: (Month, Day, Year) September 30, 1994		<b>9. Period Covered by this Report</b> From: (Month, Day, Year) July 01, 1994		To: (Month, Day, Year) September 30, 1994
<b>10. Transactions:</b>				I Previously Reported	II This Period	III Cumulative
a. Total outlays				198,798.50	637.52	199,436.02
b. Recipient share of outlays				-0-	-0-	-0-
c. Federal share of outlays				198,798.50	637.52	199,436.02
d. Total unliquidated obligations						-0-
e. Recipient share of unliquidated obligations						-0-
f. Federal share of unliquidated obligations						-0-
g. Total Federal share (Sum of lines c and f)						199,436.02
h. Total Federal funds authorized for this funding period						199,613.00
i. Unobligated balance of Federal funds (Line h minus line g)						176.98
<b>11. Indirect Expense</b>						
a. Type of Rate (Place "X" in appropriate box) <input checked="" type="checkbox"/> Provisional <input type="checkbox"/> Predetermined <input type="checkbox"/> Final <input type="checkbox"/> Fixed						
b. Rate See Attached		c. Base MTDC		d. Total Amount \$182.15		e. Federal Share \$182.15
<b>12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.</b>  <div style="text-align: right;">           Questions concerning this report should be directed to: Geraldine Reese (404) 894-2629         </div>						
GEORGIA TECH'S FISCAL YEAR ENDS JUNE 30						
<b>13. Certification:</b> I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.						
Typed or Printed Name and Title  David V. Welch, Director, Grants and Contracts Accounting					Telephone (Area code, number and extension)  (404) 894-2629	
Signature of Authorized Certifying Official  					Date Report Submitted  January 23, 1995	

Attachment

Page 2 of 2

Financial Status Report (01/23/95)

U. S. Department of Energy

Grant No. DE-FG22-90PC90293 (E-19-669/R7037-0A0)

Period Covering: 07/01/94 - 09/30/94

	<u>Direct Costs</u>	<u>Indirect Costs</u>
FY91 @ 62.5% Fixed	32,691.76	20,432.35
FY92 @ 61.5% Provisional	35,709.16	21,961.13
FY93 @ 55.2% Provisional	29,539.64	16,305.89
FY94 @ 37.0% Provisional	30,772.68	11,385.89
FY95 @ 40.0% Provisional	455.37	182.15

REPORT PERIOD

	<u>Direct Costs</u>	<u>Indirect Costs</u>
07/01/94 - 09/30/94	455.37	182.15





U. S. DEPARTMENT OF ENERGY  
NOTICE OF ENERGY RD&D PROJECTDescriptive TITLE of work  
(150 characters including spaces)

High Temperature Membranes for Hydrogen Sulfide and Sulfur Dioxide Separations

~~CONFIDENTIAL~~grant number DE-FG22-90PC90293A. MASTER contract number  
(GOCO's) \_\_\_\_\_B. Responsible PATENT office Pittsburgh, PAOriginal contract start date 090190A. Current contract start date 090190

Work STATUS

☐ Proposed ☐ Renewal  
☒ New ☐ Terminated

A. Manpower (FTE) \_\_\_\_\_

3. Performing organization CONTROL  
number (internal) E-19-669

3A. Budget and Reporting code \_\_\_\_\_

3B. Funding YEAR for this award  
19904B. Current contract close date 0831934C. Anticipated project termination  
date 0831935B. CONGRESSIONAL district 5th5C. STATE or Country where work is being  
performed Georgia

5D. COUNTRY sponsoring research \_\_\_\_\_

Name of PERFORMING organization Georgia Tech Research Institute  
Georgia Institute of Technology, School of Chemical Engineering

A. DEPARTMENT or DIVISION

School of Chemical Engineering

6B. Street Address

Georgia Institute of  
Technology

6C. City, State, Zip Code

Atlanta, Ga 30332-0100

Circle only one code for TYPE of Organization Performing R&amp;D:

- CU - College, university, or trade school
- FF - Federally funded RD&D centers or laboratory operated for an agency of the U. S. Government
- IN - Private industry
- NP - Foundation or laboratory not operated for profit
- ST - Regional, state or local government facility
- TA - Trade or professional organization
- US - Federal agency
- XX - Other
- EG - Electric or gas utility

A. Contractor's PRINCIPAL INVESTIGATOR/s or project manager  
Name/s (Last, First, MI) Winnick, Jack

B. PHONE/s (in order of PI names with commercial followed by FTS)

Comm. 404/894-2839; FTS \_\_\_\_\_; Comm. \_\_\_\_\_; FTS \_\_\_\_\_

C. PI/s address (if different from that of Performing Organization)

9. DOE SUPPORTING Organization (DOE Assistant Secretary and office sponsoring the work; technical monitor; and administrative monitor).

9A. PROGRAM division or office

(full name) Pittsburg Energy Technology Center

PM-01

Program Office Code

9B. TECHNICAL monitor (Last, First, MI) Robert Dolence

9C. Address Pittsburg Energy Technology Center 9D. Phone

Comm. 412/892-6290

P.O. Box 10940, MS 922-206

FTS

Pittsburg, PA 15236-0940

9E. ADMINISTRATIVE monitor (Last, First, MI) Dupree, Rhonda

10. FUNDING in thousands of dollars (K\$). Funds represent budget obligations for operating and capital equipment (FY runs October 1 – September 30).

Funding organization(s)	Current FY <u>1990</u>	Next FY ____
A. DOE	\$199	---
B.		
C.		

10D. Does the current FUNDING cover more than one year's work?

Yes X No \_\_\_\_

E. If yes, provide dates (from when to when). September 1, 1990 through August 31, 1993

11. Descriptive SUMMARY of work. Enter a Project Summary using complete sentences limited to 200 words covering the following: Objective(s), state project objectives quantifying where possible (e.g., "The project objective is to demonstrate 95% recovery of sulfur from raw gas with molten salt recycling at a rate of one gallon per minute."); approach, describe the technical approach used (how the work is to be done); expected product/results, describe the final products or results expected from the project and their importance and relevance.

**A high temperature membrane separation technique has been applied to gas mixtures involved in coal utilization. For coal gasification, H<sub>2</sub>S has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion, SO<sub>2</sub> has been separated from the flue gas, with concentrated SO<sub>2</sub> produced as a by-product. Both processes appear economically viable but each requires fundamental improvements: both the H<sub>2</sub>S cell and the SO<sub>2</sub> cell require more efficient membranes and the H<sub>2</sub>S cell needs a more efficient anode.**

**The membrane performance is affected by both material selection as well as fabrication technique. In this work we shall test the compatibility, both chemical and physical, of potential membrane matrix materials with the electrolyte in each application. Composition, surface, and morphology will be examined using X-ray, XAPS, and electron microscopy. Successful candidate materials will be used in creating membranes by casting procedures now extensively applied in fuel cell technology. This approach will speed the construction of multi-cell devices. For H<sub>2</sub>S removal, this will mean production of syn-gas from coal and sweetening of natural gas will proceed without the need for Claus reduction of the sulfur. For SO<sub>2</sub> removal, it will mean a simple process to replace scrubbers will provide abatement of acid rain while simultaneously producing a salable by-product.**

12. PUBLICATIONS available to the public. List the five most descriptive publications that have resulted from this project in the last year that are available to the public. (Include author, title, where published, year of publication, and any other information you have to complete full bibliographic citation.) Use the back of this form or additional sheets if necessary.

3. KEYWORDS (Listed five terms describing the technical aspects of the project. List specific chemicals and CAS number, if applicable.)

**13. a)Membranes  
b)Gas separation  
c)Electrochemical processing  
d)Ceramic membrane preparation  
e)Tape and slip-casting**

4. RESPONDENT. Name and address of person filling out the Form 538. Give telephone number, including extension (if you have FTS number, please include it) at which person can be reached. Record the date this form was completed or updated. The information in Item 14 will not be published.

Respondent's Name: Professor Jack Winnick Phone No.: 404/894-2839 Date: Sept. 5, 1990

Street: Georgia Institute of Technology

City: Atlanta State: GA Zip: 30332-0100

15. Additional space for furnishing information in items 1 to 14. (Indicate item numbers to which answers apply.)

Item No.

NOTICE: Return this form to the office indicated in the reporting requirements for your award agreement covering this project. If you have completed a similar programmatic office project description during the current Fiscal Year, complete only the new data elements on this form and send it and a copy of the description completed earlier to Department of Energy, Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831.



U. S. DEPARTMENT OF ENERGY

UNIVERSITY CONTRACTOR, GRANTEE, AND COOPERATIVE AGREEMENT  
RECOMMENDATIONS FOR ANNOUNCEMENT AND DISTRIBUTION OF DOCUMENTS

*See Instructions on Reverse Side*

1. DOE Report No. 2	3. Title High Temperature Membranes for H <sub>2</sub> S and SO <sub>2</sub> Separations
2. DOE Contract No. DE-FG22- -90PC90293	
4. Type of Document ("x" one) <input checked="" type="checkbox"/> a. Scientific and technical report <input type="checkbox"/> b. Conference paper: Title of conference _____ Date of conference _____ Exact location of conference _____ Sponsoring organization _____ <input type="checkbox"/> c. Other (Specify) _____	
5. Recommended Announcement and Distribution ("x" one) <input checked="" type="checkbox"/> a. Unrestricted unlimited distribution. <input type="checkbox"/> b. Make available only within DOE and to DOE contractors and other U. S. Government agencies and their contractors. <input type="checkbox"/> c. Other (Specify) _____	
6. Reason for Recommended Restrictions _____ _____	
7. Patent and Copyright Information: Does this information product disclose any new equipment, process, or material? <input checked="" type="checkbox"/> No <input type="checkbox"/> Yes If so, identify page nos. _____ Has an invention disclosure been submitted to DOE covering any aspect of this information product? <input type="checkbox"/> No <input type="checkbox"/> Yes If so, identify the DOE (or other) disclosure number and to whom the disclosure was submitted. Are there any patent-related objections to the release of this information product? <input type="checkbox"/> No <input type="checkbox"/> Yes If so, state these objections. Does this information product contain copyrighted material? <input type="checkbox"/> No <input type="checkbox"/> Yes If so, identify the page numbers _____ and attach the license or other authority for the government to reproduce.	
8. Submitted by Jack Winnick, Professor Organization Georgia Tech Research Corporation	
Signature _____	Phone (404) 894-2839
Date 1/20/91	

FOR DOE OR OTHER AUTHORIZED  
USE ONLY

9. Patent Clearance ("x" one)  
☐ a. DOE patent clearance has been granted by responsible DOE patent group.  
☐ b. Report has been sent to responsible DOE patent group for clearance.

Quarterly Progress Report  
Grant DE-FG22-90PC 90293  
September 1, 1990 - December 31, 1990

by

Dr. Jack Winnick  
Georgia Institute of Technology  
School of Chemical Engineering  
Atlanta, Georgia 30332-0100

Research during the period of September 1, 1990 through December 31, 1990 focused on developing a tape-casting method with several binder formulations. These formulae were based on methyl cellulose, polyvinyl butyral and acrylic as polymeric binders. Several plasticizers were used to provide a flexible tape product. Most of this work was applied towards the development of a membrane to be used in the SO<sub>2</sub> separation process.

The tape is prepared by mixing a binder/plasticizer solution and a matrix material. The matrix material for this work was finely ground borosilicate glass, chosen for its low cost and chemical stability. The polymeric binder acts to hold the matrix particles together when the tape is dried. The plasticizer gives the dried "green" tape flexibility, allowing it to be removed from the substrate and handled with ease. Surfactants or dispersants are added in small quantities to aid the coating of the matrix particles with binder. A solvent must be properly selected to dissolve the binder, plasticizer and surfactant/dispersant. The ensuing mixture of binder/plasticizer is blended with the matrix material and cast onto a suitable substrate. Proper drying rate and conditions yield a flexible tape of ceramic.

#### **A. Methyl Cellulose Binder**

The first binder/solvent system investigated was a mixture of methyl cellulose (Fisher) and distilled water. A 5 w/v methyl cellulose solution was



prepared, to which was added 6 parts of borosilicate glass per 100 ml solution. This solution was then poured into a paper-making apparatus. The solids were allowed to settle and the liquid was decanted. The solids were firmly adhered to the filter paper and the tape was not recovered.

A 2.5 w/v solution was then prepared and the same amount of borosilicate was added. Air bubbles were removed under vacuum. This solution was cast on a glass plate and leveled with a bird bar apparatus. The bird bar arrangement consists of two tracks placed along the sides of the plate, with the bird bar sliding over the tracks and tape to provide a uniformly thick tape. The tape was then air-dried to produce the green tape. The tracks are adjustable to allow for variable pour thickness. The tape produced here from a 2mm thick cast was 0.23 mm thick, showing a volume reduction of approximately 90%, closely matching the volume percentage of solvent in the cast. The green tape was easily trimmed with scissors.

Another tape was cast on glass and heated on a hot plate, to promote drying. The tape cracked as the methyl cellulose congealed. The gelation was reversed on cooling, but the cracks did not repair. Heating was not used again with methyl cellulose solutions.

A higher glass loading was used to produce the first successful tape. 10 w/v methyl cellulose was prepared, to which was added 60g of borosilicate and an

additional 80 ml H<sub>2</sub>O. A tape was cast and cracked during handling. Piece #1 had its binder burned out at 400°C and then was cooled. The required amount of electrolyte (via calculation of binder content) was placed on top and then heated to 300°C. The pores in the tape were filled, but a small puddle of excess electrolyte formed in a valley.

Piece #2 was covered with electrolyte and heated to 400°C to burn out the binder, melt the electrolyte and have it replace the binder. The electrolyte instead beaded on top, a phenomenon we have previously encountered when H<sub>2</sub>O contacts the electrolyte. The H<sub>2</sub>O comes from the combustion process and forces a change in the electrolyte composition via:



K<sub>2</sub>SO<sub>4</sub> has a high melting point, causing the beads to freeze on the exterior. This difficulty is overcome by burnout prior to electrolyte exposure.

The 10 w/v methyl cellulose solution achieved good dispersions of particles and was used for further investigations.

SiO<sub>2</sub> was also used as a tentative matrix material, but showed severe complications with hydration. Sipernat-22, a precipitated silica manufactured by Degussa, was dispersed in distilled H<sub>2</sub>O at 30 w/v to form a thick gel-like dispersion.

When tapes were cast from this formulation, they all suffered substantial cracking during drying, due to removal of H<sub>2</sub>O from the silica. This amorphous silica matrix was discarded as infeasible for aqueous-based binder systems.

Some difficulty was experienced with the tape adhering to the glass plate substrate. Other substrates such as Teflon and graphite (Grafoil) showed similar difficulties. To overcome this problem, polyethylene glycol (MW=10,000) and polyethylene oxide (MW=100,000 or 900,000) plasticizers were added to the solutions.

A mixture of 0.4 g polyethylene glycol in 20 ml H<sub>2</sub>O, 25 g of 10 w/v methyl cellulose, 13.6 g of borosilicate and 50 ml of H<sub>2</sub>O was prepared. The dispersion was very thick and deaeration proved difficult. When cast on teflon, the tape cracked, but a piece was salvaged and fired to 400°C. This product had no cracks and some strength.

To increase binder-matrix interaction, Triton N-101 was added as surfactant. To prepare the dispersion, the surfactant and matrix were first blended in water for four hours. The binder and plasticizer were then added and blended for an additional 12 hours. After deaeration, a tape was prepared, but found to suffer from incomplete mixing. More water was added and the mixture was ball-milled for 20 hours. Several tapes were manufactured with mixed success. With a glass substrate,

the tape shrunk 50% in thickness, had good appearance and was flexible. With a Grafoil substrate, the tape stuck and could not be separated.

Using the same blend, we experimented with the drying rate. To retard drying, the cast was covered, reducing the air space and convective drying. When this procedure was followed, the tapes curled towards the center, showing uneven drying from top to bottom. If drying is sufficiently retarded, settling of the ceramic occurs. This is detrimental, as the distribution of ceramic sizes settle at different rates, causing an inhomogeneous tape. However, we also found that if drying is too rapid, the surface skims, which directly causes cracking.

To increase the flexibility of the green tapes, a higher molecular weight plasticizer was investigated. 1.0 g of polythylene oxide (MW=900,00), 5.0 g of Dow Methocel (methyl cellulose) and 100 ml H<sub>2</sub>O were mixed. This solution was too thick for processing. 250 ml H<sub>2</sub>O were added to thin the mixture. 10 g borosilicate were blended and a tape was cast. A slow drying rate caused ceramic settling, but the product was very thin (0.10 mm) and very flexible. This tape was wrapped around a pencil without cracking.

In summary, several successful tapes were cast using the methyl cellulose/water system by adding a plasticizer and controlling the drying rate.

At this point, we began to investigate several commercially available binder

systems. We have procured three binder systems from Metoramic Sciences, Inc. (Carlsbad, CA). These systems are pre-mixed, with the binder, plasticizer, surfactant and solvent included. All that is required of these systems is to add the proper fraction of matrix material, blend, pour and dry. However, all of these parameters must be investigated, but some guidance is provided by the vendor literature.

#### **B. Polyvinyl Butyral Binders**

The first of the Metoramic Sciences binder solutions tested was a formulation (B73305) of polyvinyl butyral (binder) dissolved in toluene and ethanol. The binder solids content was 18.5% in the packaged solutions. According to guidelines provided, ceramic loading was at 55 volume % borosilicate. A small amount of extra solvent (10%) was added to thin the mixture and allow for full dispersion. After dispersion in a ball mill, the grinding media were removed, and the mixture was placed back on the mill to deaerate.

Several tapes were cast from this blend. The green tape stuck to the glass substrate and delaminated with low heat. Bubbles were formed between the upper and lower layers, showing that the heating rate was insufficient to prevent skimming of the upper surface. On a teflon substrate, the same results occurred. At a higher heating rate, no delamination resulted. Also, on a polyester substrate with a cover, a good green tape was formed. Due to the high level of toluene in the

binder solution, the upper surface dries quickly after pouring, causing skimming. If heat is applied, or a cover used to maintain the solvent partial pressure, skimming can be reversed and cracking prevented.

The green tapes thus formed were fired to 400°C to burn out the binder. The fired bodies retained their shape, with the exception of a few internal bubbles. All fired products had sufficient strength to permit handling, but were fragile like a ceramic.

With the initial success of these experiments, another batch of B73305 with 55 volume % borosilicate was prepared. A tape was cast onto polyester (2 mm thick) and covered to. This tape took three days to dry and suffered from some ceramic settling.

Several pieces of this tape were cut off and fired to the sintering point of borosilicate, 600°C. When slowly heated, the piece warped at 200°C as solvent and polymer were removed. After 24 hours, the oven was at 400°C and the tape was again flat. Sintering then occurred by heating for one half hour to 500°C and again to 600°C and holding for one-half hour. The piece then slowly cooled and was analyzed for shrinkage in all directions, leaving a tape which contained 28% voids. When a second piece was fired to 650°C, it shrank 15-18% and had 3% voids, by calculation. Both of these sintered tapes had porosity which we deem to be

insufficient for our process. However, the process did prove feasible for making thin sintered bodies (0.6 mm thick). A sintered body with higher porosity would be formed from lower ceramic loading and better control of the firing cycle.

### C. Acrylic Binders

Metoramic Sciences binder system B73181 uses acrylic dissolved in acetone and naphtha, along with plasticizers and other modifiers, to form a complete binder system. Blends were prepared in a high speed mixer which produced questionable dispersion. The formulation of 37 volume percent borosilicate did not stick to glass, teflon or galvanized steel and did not crack upon drying. However, agglomerates of ceramic were seen in the green bodies. Agglomerates were not seen when the blends were ball milled for sufficient time.

An experimental Metoramic Sciences binder, K565-4, was investigated because of its clean, low temperature burnout properties. These properties are beneficial for electrolyte tapes, as the finished tapes are expected to be stacked in the test cell, fired for burnout, and then evaluated. The binder system consists of acrylic dissolved in heptane and isopropanol, with other additives. When combined with borosilicate, the cast tapes adhered to teflon, polyester and glass, without cracking. Unfortunately, none of the tapes could be recovered for further testing.

A blend of 55 volume percent electrolyte (5 wt %  $V_2O_5$  in  $K_2S_2O_7$ ) was

prepared. A release agent was added to the blend to aid removal of the green tape from the substrate. When cast and slowly dried, the tape still stuck to the glass substrate. Since the drying cycle took six days, it is believed that the modifier had evaporated.

#### **D. Full Cell Evaluation**

Several of the successful tapes were tested in the full cell apparatus with simulated flue gas flowing over both electrodes. Electrolyte was added in powder form between the electrodes and tape.

A tape prepared with methyl cellulose binder and polyethylene glycol plasticizer was measured and weighed to determine the volumes occupied by solids and binder. The amount of electrolyte required to fill the binder voids was added, the cell was assembled and heated to 400°C. During this test, a good seal was established around the periphery of the cell housing. The polarization performance was quite poor due to a high electrolyte electrical resistance. This is thought to be caused by high levels of  $K_2SO_4$  formed during binder burnout (equations 1 and 2).

This test was duplicated with another tape from the same batch. During burnout, pure oxygen was used instead of flue gas. In this run, ultra-thin gold screens were used as electrodes to reduce concentration polarization effects found in the porous gas-diffusion perovskite electrodes. This run suffered intermittent



electrical shorting between the anode and cathode, but overall was a great success. Current equal to 95% removal of  $\text{SO}_x$  was supported with 1.5 V. Additionally, the electrode potential rapidly responded to changes in the gas flow rate over either electrode with current applied. This experiment proved the feasibility of tape casting the matrix and showed that the majority of concentration polarization previously experienced probably lies in the porous perovskite electrodes. Replacement or alteration of the perovskite electrodes is being evaluated separately.

Three full cell experiments were conducted using a knitted zirconia fabric (Zircar). This flexible fabric is made from yttria-stabilized zirconia (8 wt %  $\text{Y}_2\text{O}_3$ ) and has properties of 85% porosity, 0.015" (0.38 mm) thickness and zero volatiles. The pore distribution is bimodal, with one peak at 10 microns and the second at 30 microns. This fabric has been used in high temperature and corrosive environments, such as molten alkali chlorides and carbonates. On this account, it should hold promise for our applications.

A square of fabric was cut to fit the cell, weighed and the required amount of potassium pyrosulfate electrolyte calculated. This electrolyte was added between the electrode and fabric. The cell was assembled and operated. Observations showed that some gas crossover was present, along with a high electrolyte resistance. Although additional electrolyte was added, these problems were not fully solved, so

the run was terminated. Post-mortem analysis showed the porous perovskite electrodes gained weight, drying out the membrane and allowing the problems cited above to continue.

A second run with this fabric contained an initial excess of electrolyte, in the amount required to fill the electrodes. Good housing seals were formed, along with no gas crossover. Cell resistance was reduced, compared to the previous run, but not to the required level.

A third run, using the electrolyte-laden electrodes from the previous run, was conducted and showed lower cell resistance. Over time, this resistance increased but could be corrected with electrolyte additions. After the run, the zirconia fabric was ground and analyzed via x-ray powder diffraction. A new phase was present, but at a concentration too low for detection. This analysis will be continued at a later date.

#### **E. H<sub>2</sub>S Separation Process**

Work in membrane development for the H<sub>2</sub>S separator process has been concentrated in two areas. These were utilization of Metoramic's ceramic binder systems to produce flexible 'green tapes' of MgO, as opposed to the borosilicate tapes made for the SO<sub>2</sub> separation process, and work with full cell experiments using Zircar's woven zirconia cloths as a matrix material in the separator membranes.

Metoramic's binder system B73305 was successfully used to manufacture

approximately 0.4 mm thick 'green tapes' of MgO at a ceramic loading level of 43%. Three of these tapes were cut to shape (3" diameter circles) and laminated together under 8000 psi to form a single 1.2 mm thick 'green tape'. The organic binders were then volitized at 520°C under dry N<sub>2</sub> over an 8 hour period. The resulting ceramic body (unsintered) had a porosity of 82%. Work will continue in the forming of an electrolyte tape which can be laminated to the ceramic tape which, upon volitalization of the organic binders, will be infiltrated into the voids of the resulting ceramic body at cell operating temperatures.

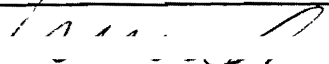
Zircar's woven zirconia cloth has been identified as an alternative matrix material for full cell laboratory ZWY-30A scale tests. The cloth has a porosity of 83% and a thickness of 0.8 mm. The average pore size is reported by the company as 10  $\mu$ m which is small enough to retain the electrolyte by capillary action. Laboratory runs of the full cell have been maintained as long as 219 hrs using this matrix material and back pressures as high as 8" H<sub>2</sub>O have been measured with no bulk gas cross-over from the process to the sweep sides of the cell.

Experiments on in-situ impregnation of matrix materials have been successfully carried out in full operating cells with both Zircar's woven zirconia cloths and sintered MgO matrixes.

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**Quarterly Progress Report**  
**Grant DE-FG22-90PC 90293**  
**January 1, 1991 - April 30, 1991**

**by**

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## A: SO<sub>x</sub> Removal Cell

### Summary

Several major accomplishments were achieved during the present reporting period. First, a viable electrode was identified and tested, both for stability and cell performance. Second, particle size distributions were determined for the candidate matrix materials, allowing a better understanding of which materials will yield high quality membranes. Third, a long duration run was completed at substantially higher current densities, proving the effectiveness of Si<sub>3</sub>N<sub>4</sub> as a matrix and the lithiated nickel oxide as an electrode.

### I. Electrode Work

Although the present research does not focus on electrode development, previous experiments confirmed that a new electrode was required to permit further development of the SO<sub>x</sub> removal process. A brief description of this work follows.

Many metals were investigated as electrode replacements, including stainless steels (SS 304, 347 and 430), oxidation-resistant alloys (Haynes 188 and Hastelloy-X) and nickel or lithiated nickel oxide. These materials were tested because they are commercially available in fibrous mesh form. Testing included cyclic voltammetry (CV) for corrosion resistance in the molten pyrosulfate (K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>) and longer duration stability tests, where samples were exposed to the molten salt and weight changes determined. The lithiated nickel oxide (a common molten carbonate fuel cell cathode material) was manufactured by soaking nickel mesh in 1M LiOH and heating to 600° C to form the lithiated nickel oxide. This structure was confirmed by X-ray powder diffraction, with the remaining phase being unoxidized nickel.

Of all the materials examined, lithiated nickel oxide appears to be the best. A CV on clean nickel wire showed a distinct oxidation peak, corresponding to the formation of NiO. After testing, the wire had gained an oxide coating on the area exposed to the melt. A CV on lithiated NiO mesh showed no oxidation peak. This test showed the electrochemical corrosion did not occur, but gave no conclusions as to chemical corrosion. Stability tests showed the formation of small amounts of  $\text{NiSO}_4$ , a corrosion product. This product is non-conductive, but no decrease in performance was seen during CVs and full cell tests (described below). The sulfates may be due to corrosion of either NiO or exposed Ni surfaces. Further evaluation continues on lithiated nickel oxide, but its polarization performance, with any membrane structure, is much better than the previously used perovskite electrodes,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  or  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_3$ . Much of this improvement is due to the higher porosity (95%) and lower surface area enhancement (actual = 12x superficial) compared with the perovskites (55% porous, 200x surface area enhancement). These factors reduce the possibility of electrode pore flooding.

## **II. Particle Size Analyses**

Particle size analyses were conducted on several candidate matrix materials. These included a zeolite, ZSM-5 (Silicalite), two borosilicate glass preparations, two silicon carbide materials, two silicon nitride materials, titania (anatase  $\text{TiO}_2$ ), crystalline silica ( $\text{SiO}_2$ ), zirconia ( $\text{ZrO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ).

The SiC and  $\text{Si}_3\text{N}_4$  samples failed to give proper analysis, as confirmed by their

manufacturer, Phillips Petroleum (Bartlesville, OK). Sample preparation failed to break up the agglomerates of these fine particles. Actual particle size distributions were obtained from Phillips, but cannot be disclosed due to a secrecy agreement.

Results are tabulated in Table I. The median particle size (volume basis) shows

**Table I. Particle Size Analyses**

Material	Median Diameter, $\mu\text{m}$
Silicalite	3.83
Glass, milled 6 days	4.81
Glass, milled 7 days	4.72
Titania ( $\text{TiO}_2$ )	1.35
Silica ( $\text{SiO}_2$ )	3.0
Zirconia ( $\text{ZrO}_2$ )	15.0
Alumina ( $\text{Al}_2\text{O}_3$ )	0.84

that some materials are better suited for matrix purposes, with median diameters near  $1\mu\text{m}$ . Earlier work showed that the matrix should be an order of magnitude smaller than the electrode pores, which are ideally  $\sim 10\mu\text{m}$ . The unpublished data on the Phillips Petroleum ceramics shows them to be ideally suited for use as matrix materials, with very narrow distributions of ideal median diameter.

The borosilicate glass materials were prepared by wet milling <325 mesh (<44 microns) glass for 6 or 7 days. In addition, chemical stability tests have shown the titania and zirconia (in the pure form, not as fabric) to be stable, whereas the silica and alumina react.



### **III. Membranes**

#### **A. Borosilicate Glass**

Several tapes were cast from a blend of 45 volume percent (v/o) glass in vinyl butyral binder (Metoramic B73305). Varying results were found upon burnout, depending on drying conditions. Some tapes dried too rapidly, causing minor mud cracks on the surface. These mud cracks caused cracking of the membranes upon heating to  $T > 450^{\circ} \text{C}$ . When drying conditions were better controlled, no cracking resulted in the membrane, allowing complete wetting of the matrix with electrolyte.

#### **B. 55 v/o $\text{Si}_3\text{N}_4$ tapes**

Several tapes were cast from a blend of Phillips Petroleum  $\text{Si}_3\text{N}_4$  (SN-P) and vinyl butyral (B73305). Initial work with this matrix failed to produce satisfactory tapes for two reasons: 1) the surface area of the matrix was twice that used to calculate the binder loading, and 2) the blend was not well dispersed. Later tapes overcame this problem by adding more polymer and using a sonicator to break up the agglomerates. Additional surfactant also helped to overcome the problem. When poured onto the substrate, very flexible 0.4 mm thick tapes were produced reproducibly. One of these tapes was run in the full cell, as described below.

#### **C. 45 v/o $\text{Si}_3\text{N}_4$ tapes**

After a successful run with the 55 v/o  $\text{Si}_3\text{N}_4$  tape, a set of tapes was made at 45 v/o ceramic in vinyl butyral (B73305). Two tapes were laminated at 700 psi to form a uniform membrane. This tape was run with great success in combination with the lithiated NiO electrodes, as documented below.

## **IV. Full Cell Tests**

### **A. Zircar Zirconia Fabrics**

Two full cell tests were conducted during this quarter with Zircar fabrics. The fabric is made from yttria-stabilized (8 w/o  $Y_2O_3$ ) zirconia, in either knitted or woven form. Since these materials worked well in the  $H_2S$  removal process, preventing gas crossover and retaining sufficient electrolyte, they were tested here.

During full cell testing, performance of the fabric decayed over time. Cell resistance increased, to the point of prohibiting passage of current. Post-mortem analysis showed the fabric to react with the  $K_2S_2O_7$  electrolyte, leaving the electrolyte phase enriched in  $K_2SO_4$ . The remaining membrane was water soluble, confirming the reaction of the fabric, with the formation of water soluble zirconyl sulfates. These fabrics were dismissed as viable membrane matrices.

### **B. Borosilicate Glass**

A 55 v/o borosilicate glass tape was prepared from 6-day milled glass and vinyl butyral binder (B73305). This tape was installed in the cell with a disc of electrolyte above. Lithiated NiO mesh and  $La_{0.8}Sr_{0.2}CuO_3$  electrodes were used to compare their performance. To remove the polymeric binder in the tape, the cell was heated with pure  $O_2$  flowing past both electrodes. Unfortunately, the electrolyte melted before burnout was completed and the molten electrolyte ran out of the cell. This situation was remedied by adding new electrolyte through the reference electrode port.

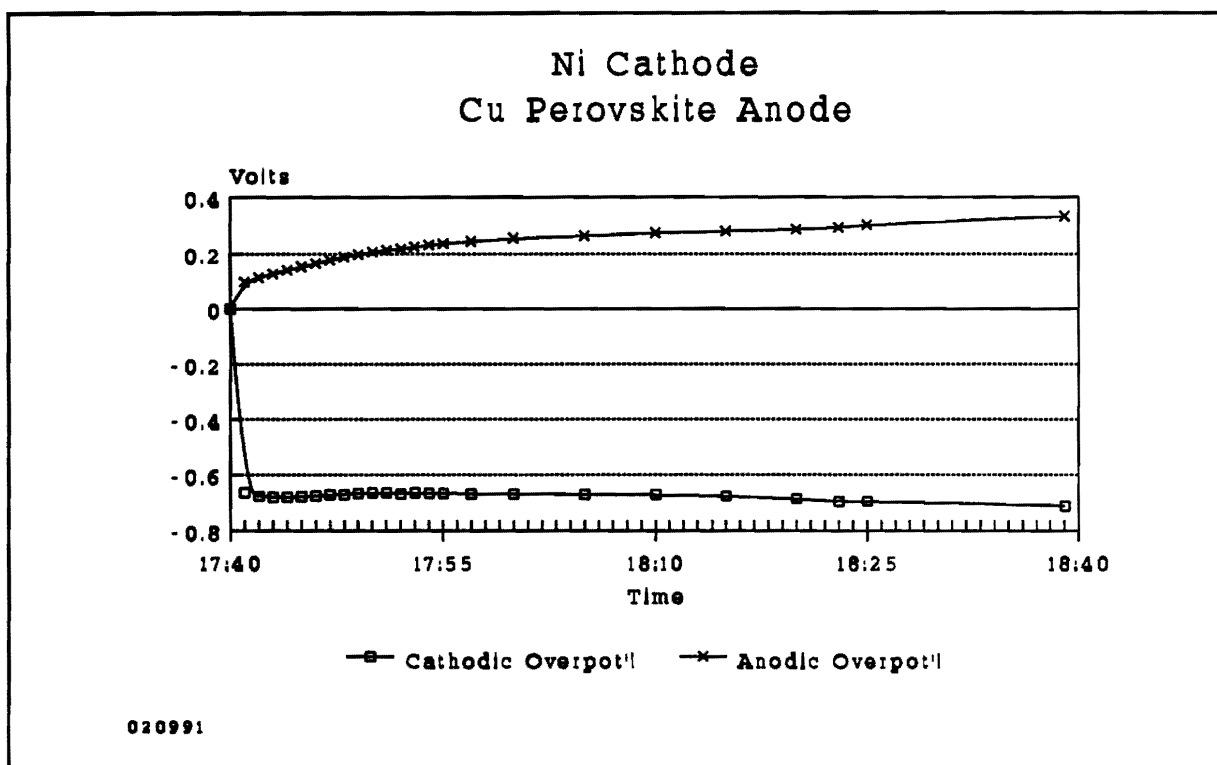
Constant-current experiments with sufficient gas flow showed that the  $La_{0.8}Sr_{0.2}CuO_3$ , as an anode, decreases in polarization performance over time, whereas

the lithiated NiO maintains, if not improves, its polarization performance. (Compare Figures 1 & 2, which show lower cathodic overpotential in Fig. 2, conducted two days after Figure 1). After these experiments, the current polarity was switched, making the NiO the anode and the Cu-based perovskite the cathode. Figure 3 shows that the lithiated NiO electrode performs much better than the Cu-based perovskite as a cathode. Even as an anode, the lithiated NiO performs well.

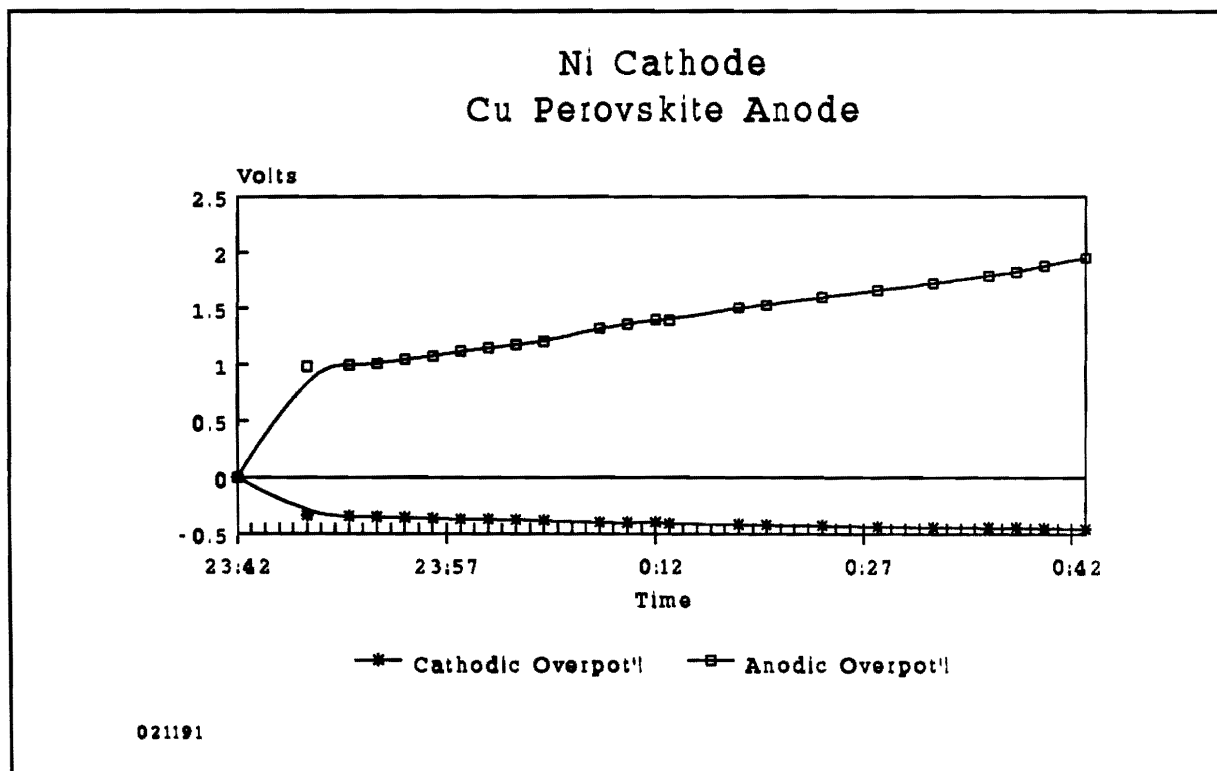
### **C. Hot-pressed MgO**

A full cell test was conducted with lithiated nickel oxide electrodes and a conventional MgO-based hot pressed membrane. The membrane was not ideal, at 80% of theoretical density, but performed quite well. This study was conducted to compare electrode performance on an established membrane structure. Although the polarization performance was not as good as in the previous study, the cell was stable with current applied for over four hours, an improvement over previous configurations. SO<sub>x</sub> removals of up to 74% were recorded at a current equal to 90% removal of inlet SO<sub>2</sub>. The electrodes were responsive to gas flow rate changes, showing that the structure was not flooded. The membrane had a relatively high ionic resistance, due to its low density. The cell finally failed from corrosion of the Ni lead wires in the gas outlet tubes. This corrosion occurred where the gas temperature decreased below the H<sub>2</sub>O and SO<sub>3</sub> condensation points. Later studies used gold or platinum contact and lead wires to stop this problem. No electrical problems were encountered inside the cell.

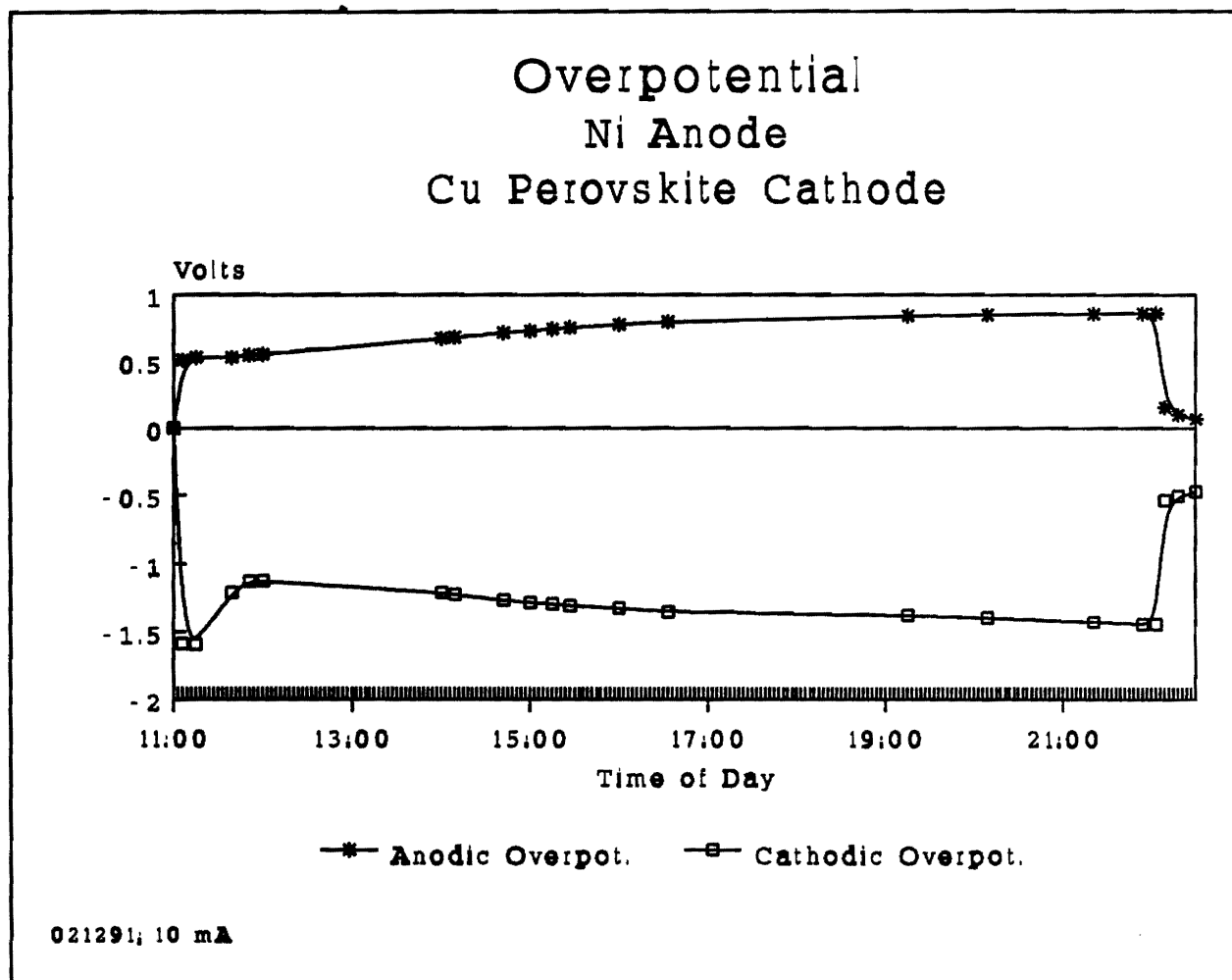
### **D. 55 % Si<sub>3</sub>N<sub>4</sub> membrane**



**Figure 1.** Cell electrode overpotentials at 400° C, 10 mA.



**Figure 2.** Cell electrode overpotentials at 400° C, 10 mA.



**Figure 3.** Polarization for cell electrodes at 400° C, 10 mA applied current. 76 ml/min of 0.3% SO<sub>2</sub>, 3% O<sub>2</sub> in N<sub>2</sub>.

This membrane formulation was tested in the full cell with the new lithiated nickel oxide electrodes. The tape was burned out on top of the bottom housing with pure  $O_2$  over a 12 hour period, up to  $400^\circ C$ . Electrolyte was melted in a crucible and added to the exposed upper surface and allowed to penetrate the membrane structure before the top housing was installed. At this point,  $O_2$  was replaced with flue gas at both sides of the membrane.

Current densities of up to 100 mA were successfully applied. Upon post-mortem, the cathode was found to be fully wetted ( $20\text{ cm}^2$  superficial area), while the anode was one-half wetted ( $10\text{ cm}^2$ ). Therefore the current densities at the anode are twice those of the cathode, causing the anode to have higher polarizations than expected. The cathode successfully sustained current densities of up to  $5\text{ mA/cm}^2$ .

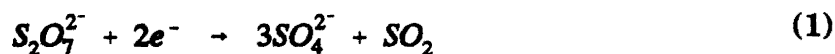
#### **E. 45 % $Si_3N_4$ membrane**

##### **Removal Performance**

A laminated two-tape membrane was tested with lithiated NiO electrodes, achieving higher current densities and good polarization. The cell still produced quality data after 28 days on-line, compared to very early experiments which produced quality data for only three or four days. Most of this endurance came from the use of a chemically stable electrode material.

This configuration was very efficient at removing  $SO_3$ , showing visible decreases in the cathode exit plume three minutes after current was applied. A net generation of  $SO_3$  at the anode was also detected within the first several minutes. Removal of 72% of inlet  $SO_x$  was achieved with current equal to 90% removal (50

mA). The residual  $\text{SO}_x$  detected in the outlet stream was partially in the form of  $\text{SO}_2$ , coming from the electrochemical reduction of  $\text{K}_2\text{S}_2\text{O}_7$  (1). At low current densities, this



generation was not a problem, but as current densities exceeded  $1.0 \text{ mA/cm}^2$ ,  $\text{SO}_2$  generation became detectable. As the current density is increased, the gas flow increases in a linear fashion, sweeping the generated  $\text{SO}_2$  away from the electrode surface.

The  $\text{SO}_2$  generation was seen to increase with increasing current. At 50 mA, with 90% removal current equal to 100 mA,  $\text{SO}_x$  removal was 72%. The removal was in excess of 45% because of residual removal (30%) at open circuit. This phenomena always occurs if the electrolyte contains excess sulfate. When the current was doubled to that equal to 90% removal, removal dropped to 56%. During this run,  $\text{SO}_3$  was barely visible in the cathode outlet stream at 100 mA, confirming the presence of higher levels of  $\text{SO}_2$  in the effluent. An on-line  $\text{SO}_2$  analyzer will be installed in the future to quantitatively determine the relation between current, flow rate and  $\text{SO}_2$  generation.

At  $5 \text{ mA/cm}^2$ , the incoming gas stream (275 ml/min, 36 cm/sec superficial velocity) did not remain in the inlet tubes long enough to provide adequate heating. The gas then enters the Pt pre-oxidation catalyst bed below  $400^\circ \text{C}$ , kinetically preventing equilibrium conversion to  $\text{SO}_3$  (99%  $\text{SO}_3$ ). Also, since the gas enters the cell cold, it chills the surface of the electrode, causing partial freezing of the  $\text{SO}_4^{2-}$

enriched catholyte, increasing the polarization at the cathode. This chilling of the electrode surface may also be the cause of the  $\text{SO}_2$  generation, as the  $\text{V}_2\text{O}_5$  in the electrolyte film will not be active enough towards  $\text{SO}_2$  oxidation at slightly reduced temperatures. The oxidation of the inlet  $\text{SO}_2$  was solved by installing an auxillary reactor, towards the end of this run, to convert the  $\text{SO}_2$  to  $\text{SO}_3$  before entering the cell. This did not solve the problem of  $\text{SO}_2$  generation, because the gas partially cooled between the auxillary reactor and the cell entrance. A modified cell design, allowing longer residence time in the heated tubes, should stop this problem.

After the auxillary reactor was installed, several applied current experiments were applied. Although the results exhibited the same general trend of  $\text{SO}_2$  generation with increasing current, removals were several percentage points higher using the auxillary reactor, but not outside the range of experimental error.  $\text{SO}_2$  generation was quantified via gas chromatography, and showed that above 20 mA current,  $\text{SO}_2$  was present in the cathode outlet stream, at a level of ~13% of inlet concentration.

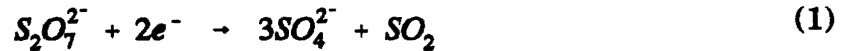
Currents as high as 200 mA ( $10.8 \text{ mA/cm}^2$  at the cathode) were reached for 10 minutes (after 3 hours at 100 mA), but with unacceptable voltages (-4.4V at cathode, +9V at anode) due to the cool gas stream and low  $\text{SO}_2$  oxidation mentioned above.

### Polarization Performace

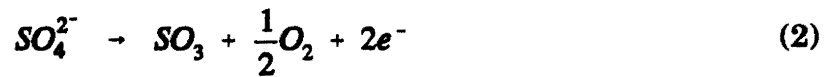
Only minor degradation in performance was detected over the 28 day period. The electrolyte membrane did show some decay in performance, as measured by solution resistance and gas crossover. Many of the experiments were conducted at



current levels above the system's ability to remove  $\text{SO}_x$ , due to the previously mentioned limitations. This had the effect of a net consumption of electrolyte through the electrochemical reactions at both the cathode and anode. The cathodic reaction (1) can result in a net loss if the generated  $\text{SO}_2$  is not oxidized, as seen in this



experiment. The anodic reaction (2) can also consume electrolyte, since it proceeds



unimpeded. After running above removal limitations, the membrane is "dried", increasing resistance and eventually allowing gas crossover.

When gas crossover was seen, additional electrolyte was added, with the effect of stopping crossover, but with no effect on polarization. In a cell with high surface area enhancement electrodes, excess electrolyte has the effect of flooding electrode pores and increasing polarization. Because the present electrodes have a low enhancement factor (12x), excess electrolyte did not cause pore flooding. Any excess that could not be held in the membrane ran out the sides of the cell.

Overpotential behavior for all runs was very reproducible. Figures 4 and 5 demonstrate the reproducibility of the data, with only a minor shift in the initial anodic behavior between runs. The cathodic drift to more negative potentials over time shows a gradual accumulation of  $\text{SO}_4^{2-}$  on the electrode, due to the less than theoretical removals (described earlier).

A standard polarization curve of overpotential versus applied current density is shown in Figure 6 for the present cell in comparison with previous cells. Note that

### Li-NiO electrodes & Si<sub>3</sub>N<sub>4</sub> Laminated Tape

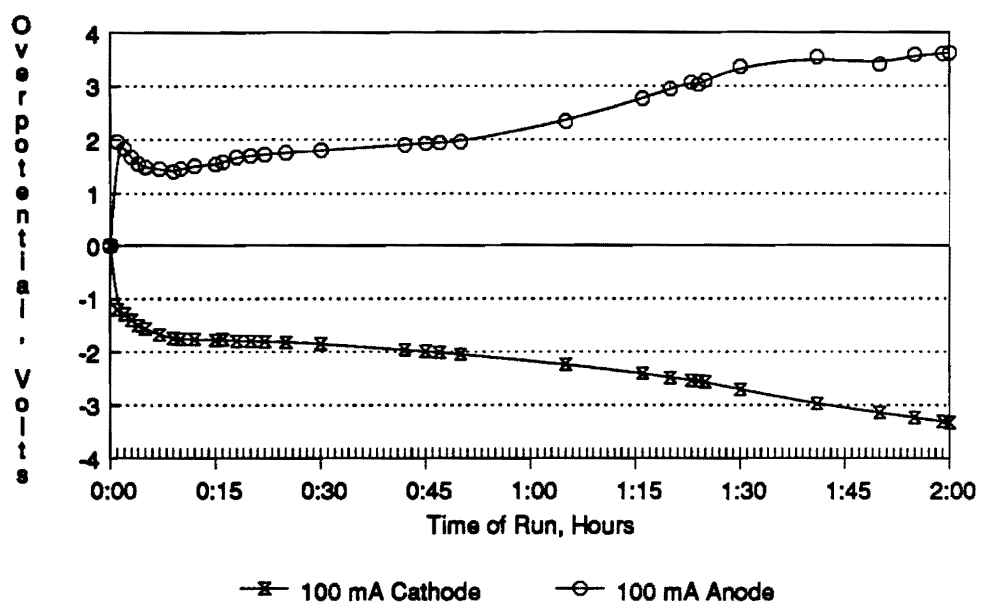


Figure 4. Overpotentials during run.  
032491 & 032591

### Li-NiO electrodes & Si<sub>3</sub>N<sub>4</sub> Laminated Tape

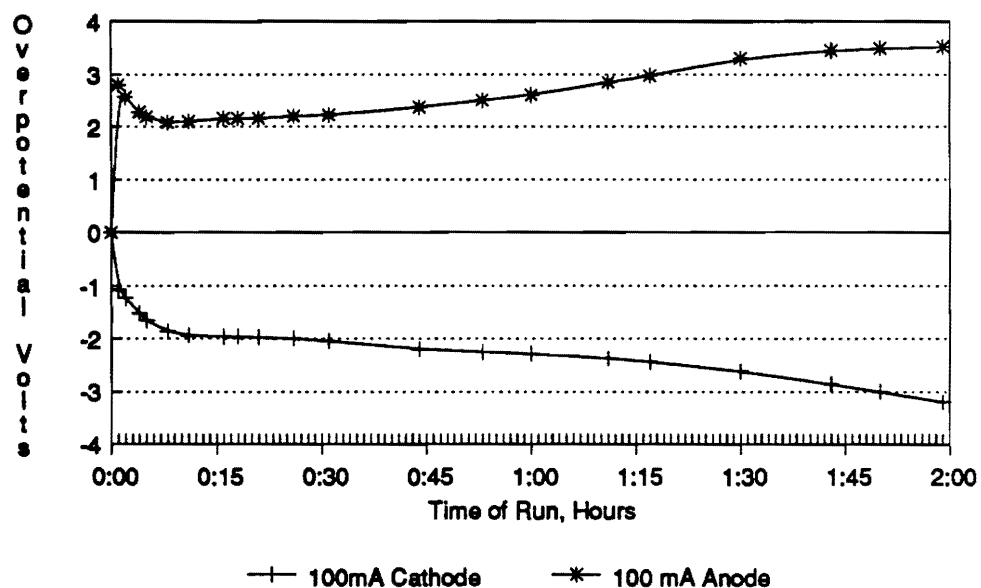


Figure 5. Overpotentials during run.  
032891

# Cathodic Polarization

## Li-NiO electrodes and various membranes

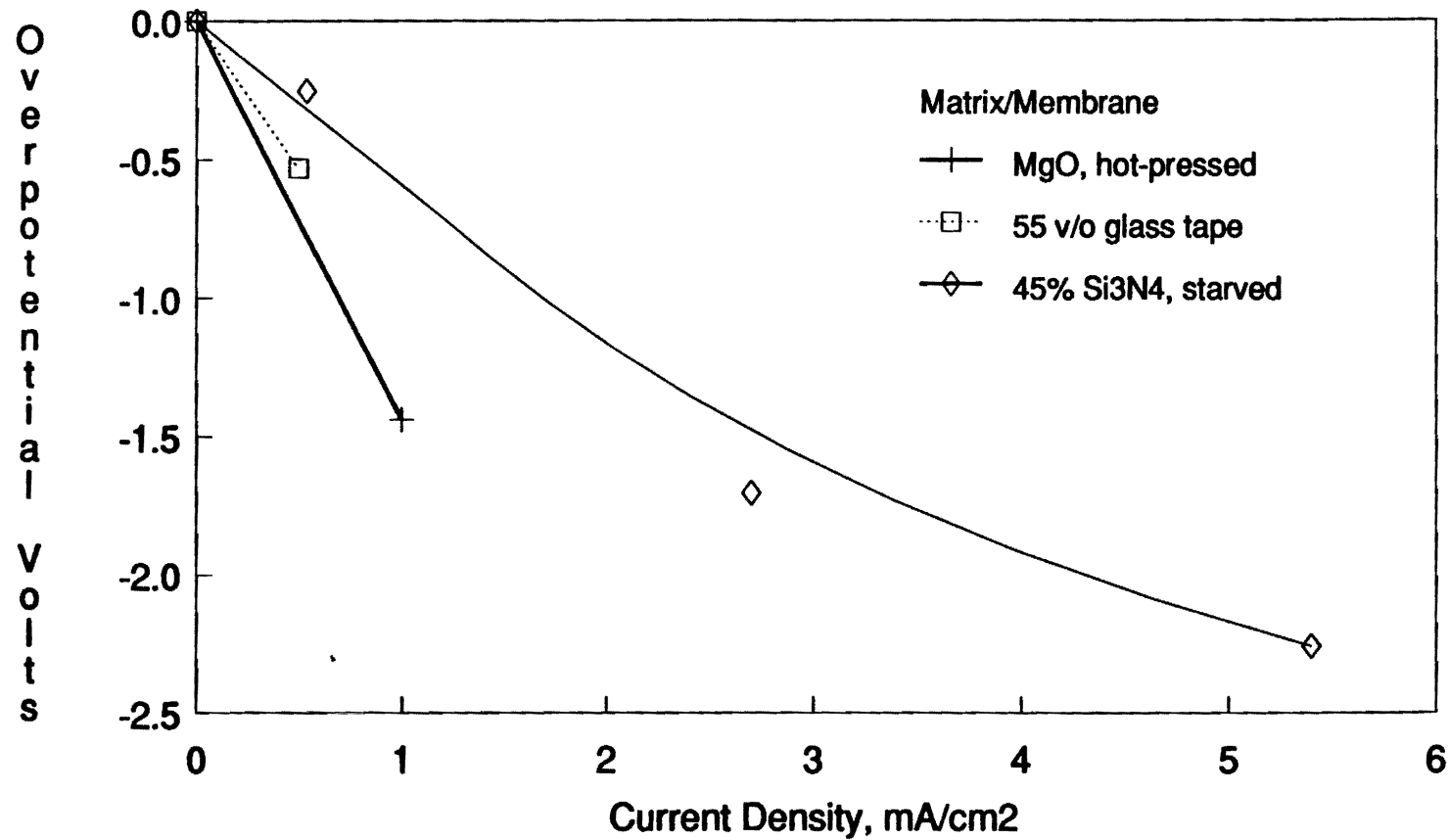


Figure 6.  
IR = 0.5 - 5.5 Ohms Cathode to Reference  
Current on for 60 mins; 400 deg. C.

the present configuration, with 45%  $\text{Si}_3\text{N}_4$  and no flooding, shows substantial improvement in polarization performance over the other membranes. Five times as much current was passed with only a 50% increase in overvoltage driving force. This shows that the proper selection of matrix material and processing conditions can result in substantial performance increases, even with the above mentioned problems.

### Post-Mortem Analysis

X-ray powder diffraction analysis of the cell components was conducted. The cathode had several phases present, predominately  $\text{LiNiO}_2$ , with some  $\text{NiO}$  and  $\text{K}_2\text{Ni}_2(\text{SO}_4)_3$ . The sulfate phase was present in approximately the same proportion as found in the stability tests mentioned above. The anode contained much more of the  $\text{K}_2\text{Ni}_2(\text{SO}_4)_3$ . No significant decrease in conductivity was found at the end of the run, even though non-conductive sulfates were present. It is unclear whether the sulfates result from corrosion of exposed  $\text{Ni}$  or  $\text{SO}_3$  attack of  $\text{NiO}$ . The thermal expansion coefficients of  $\text{Ni}$  and  $\text{NiO}$  are very different, so that upon heating, some of the  $\text{NiO}$  may have separated, leaving  $\text{Ni}$  fibers exposed. The membrane showed  $\text{KHSO}_4$ ,  $\text{Si}_3\text{N}_4$  and  $\text{K}_2\text{Ni}_2(\text{SO}_4)_3$ . The presence of  $\text{Ni}$  is explained by the high level of electrode material stuck to the membrane. Further analysis will be performed on the  $\text{Si}_3\text{N}_4$  to determine its stability.

Further research should allow us to remove the problems of heat transfer and  $\text{SO}_2$  oxidation, allowing us to push the cell to higher currents and hopefully better polarization. The next scheduled full cell run will be with a fully lithiated molten carbonate fuel cell  $\text{NiO}$  electrode. This material has a lower porosity and a higher

surface area enhancement factor. Through proper selection of electrode and membrane porosities, higher current densities should be achieved with reasonable overpotentials.

## **B: H<sub>2</sub>S Removal Cell**

### **Summary**

Work has continued on development of a H<sub>2</sub> gas-impermeable membrane for use in the H<sub>2</sub>S removal cell. A composite matrix of tape cast MgO and zirconia cloth purchased from Zircar has been used with success in a completely selective H<sub>2</sub>S removal cell, thus indicating that H<sub>2</sub> diffusion through the membrane had been prevented. The electrochemical cell system has also been used in polishing applications and has successfully removed H<sub>2</sub>S from 100 ppm down to 5 ppm.

### **I. Membrane Development**

Further refinement of the tape casting technique for production of ceramic matrixes in the removal cell membranes took place. Metoramic's binder system K565-4, an acrylic based system has shown the best results. Slurries of 20.5 wt% MgO, 78.5 wt% K565-4, 0.9 wt% M-1111 (Metoramic's releasing agent), 0.9 wt% M-1114 (Metoramic's dispersing agent) were cast on a glass substrate which had been coated with Metoramic's M-1111. This produced a tape which could be cut into seven three inch diameter circles with a thickness of 0.4 mm.

Lithium/potassium carbonate (with a cation ratio corresponding to the low

melting point eutectic,  $\text{Li}_{0.62}\text{K}_{0.38}$ ) was also mixed with K565-4 at a level of 20.8 wt% electrolyte to 79.2 wt% K565-4 binder system. This slurry was also drawn down onto M-1111 coated glass. This dried to form a tape which was 51.7 wt% electrolyte and 48.3 wt% binder.

An attempt was made at operating a cell using a membrane which was composed entirely of tape cast materials. Two electrolyte tapes were laminated with two MgO matrix material tapes and the resulting structure was loaded into the cell apparatus for heat-up and testing. The matrix failed, however since too much pressure was placed on the cell housings during heat-up to the binder volatilization temperature. The membrane extruded from the cell as the binders softened.

A densified membrane which used tape cast MgO layered with zirconia cloths was also used. Here three tapes of MgO were layered with three mats of ZYW-30A zirconia cloth from Zircar. This provided a  $\text{H}_2$  gas impermeable matrix.

## **II. Run Summaries**

### **Run 36**

This experimental run used a membrane made of tape cast materials. As was mentioned above, two tapes of electrolyte material were laminated with two tapes of MgO. The cell was loaded into the furnace and compressed under a pressure of 10 psi with a 1/2" pneumatic ram.  $\text{N}_2$  sweep was started to both the cathode and the anode sides of the cell and the furnace was heated to 350 °C over a two hour period of time. Gas seals between the MACOR housings and the membrane were perfect at

this point. As the temperature continued to rise, however, the cell seals became worse until finally there were almost no cell seals at all. After heating up to 550 °C over a four hour period, the cell had completely shorted out, as indicated by the application of current giving only electrode resistance effects on the oscilloscope. The cell was shut down at this point and it was seen that all membrane material had extruded from the cell, leaving no membrane between the electrodes.

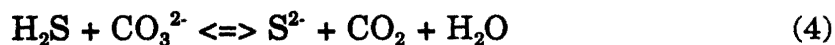
### Run 37

This run was an attempt at using the removal cell for a polishing application. A process gas with a composition of 100 ppm H<sub>2</sub>S, 1.5% CO<sub>2</sub>, and 3.2% H<sub>2</sub>O was supplied to the cathode. N<sub>2</sub> was supplied as an anode sweep. The membrane was two mats of ZYW-30A zirconia cloth soaked with 97% carbonate, 3% sulfide electrolyte (Li<sub>0.62</sub>K<sub>0.38</sub>). The cathode was carbon and the anode was CoS<sub>2</sub>. A flame photometric detector was installed on the gas chromatograph for analysis of low levels of H<sub>2</sub>S and infrared CO<sub>2</sub> analysis units were installed in the downstream cathode and anode flow lines.

Examination of Figure 7 shows the zero current basis removals of H<sub>2</sub>S and CO<sub>2</sub> as a function of current. Zero current basis removal is defined as follows:

$$\%Removal_{zerobasis} = \left[ \frac{(\text{Exit Conc.}_{zerocurrent} - \text{Exit Conc.}_{currentappl.})}{(\text{Exit Conc.}_{zerocurrent})} \right] * 100 \quad (3)$$

Since there is some scrubbing effect on H<sub>2</sub>S by the electrolyte if the sulfide concentration in the electrolyte is low by:



zero current basis removal compensates for this scrubbing effect and only reports the electrochemical effects on species removal. It can be seen from Figure 7 that  $\text{H}_2\text{S}$  removal is preferential to  $\text{CO}_2$  removal, even though  $\text{CO}_2$  is present at three orders of magnitude higher concentrations than  $\text{H}_2\text{S}$ .

Figure 8 shows the electrode overpotentials versus current. Examination of this data shows that cell overpotentials remained below the 1 volt threshold for  $\text{CO}_2$  removal up to applied currents of 300 mA. However, the fact that  $\text{CO}_2$  was transported anyway shows that  $\text{H}_2$  cross-over was present.

### Rup 38

This experimental run was the second polishing application run and used three mats of ZYW-30A zirconia cloth layered with three tapes of MgO ceramic as a membrane material. The MgO was present as a densifier for the membrane matrix to prevent  $\text{H}_2$  cross-over and subsequent transport of  $\text{CO}_2$  across the cell. The electrolyte was lithium/potassium carbonate eutectic and was layered into the membrane during set-up. Both the cathode and the anode in this experiment were  $\text{CoS}_2$ .

A nitrogen sweep was applied to both sides of the cell and the cell was loaded into the furnace for heat-up. The binder from the MgO tapes was volatilized out at  $375^\circ\text{C}$  overnight. The pressure on the pneumatic ram was only 2.5 psi during volatilization and was increased to 5 psi once run temperature was reached.

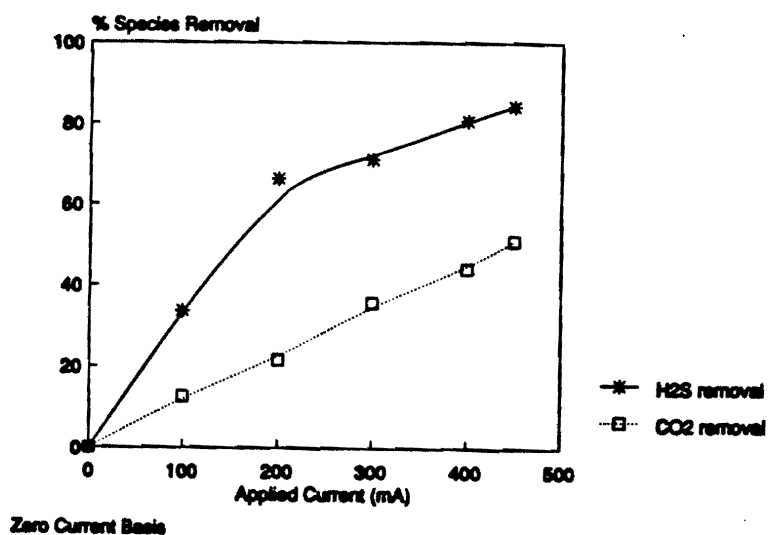


Examination of the data presented in Figure 9 shows that the densification of the matrix appears to have worked. Completely selective removal of  $\text{H}_2\text{S}$  from the process gas appears to have been achieved. The overpotential data presented in Figure 10 shows that the 1 volt cross-cell potential threshold was never crossed during the period of time that this data was taken. Future work will verify these results. No elemental sulfur was collected. Since the concentration of  $\text{H}_2\text{S}$  was so low, a negligible amount of sulfur would have been produced. The cell ran for 130 hours and was shut down due to break-down of the anode, probably due to the slow oxidation of  $\text{CoS}_2$  at higher potentials. With transport of  $\text{CO}_2$  at higher potentials,  $\text{O}_2$  would also have been produced, reacting with the  $\text{CoS}_2$  to form cobalt oxide species and sulfur dioxide. Since cobalt oxide is not conductive, this would have driven the anodic overpotential higher and thus made the situation worse, increasing the rate of cobalt oxidation. This situation was observed, with rapid decay of the cobalt disulfide anode once  $\text{CO}_2$  transport started and a possible sulfur dioxide peak appearing in the anode sweep gas chromatograph (this has not yet been verified with calibration standards, but the signal was retained too long in the column to have been  $\text{H}_2\text{S}$  or  $\text{COS}$ ).

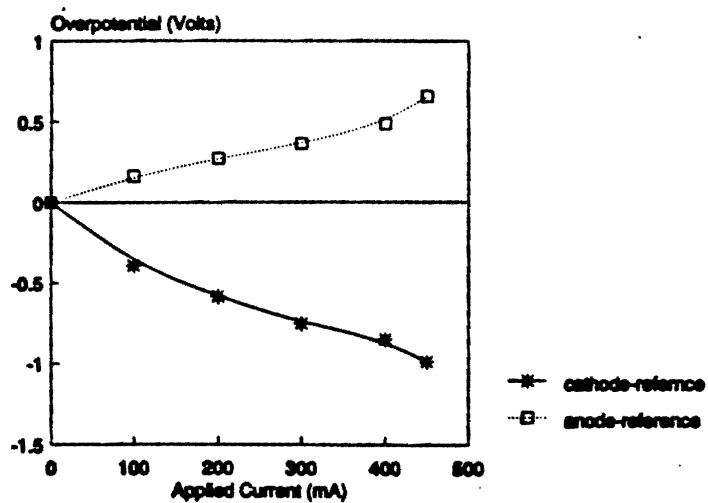
### **III. Future Work**

Work during the next quarter will center around verifying the completely selective  $\text{H}_2\text{S}$  removal results of Run 38 and experiments with lithiated nickel electrode materials. Lithiated nickel should work well as an anode material since

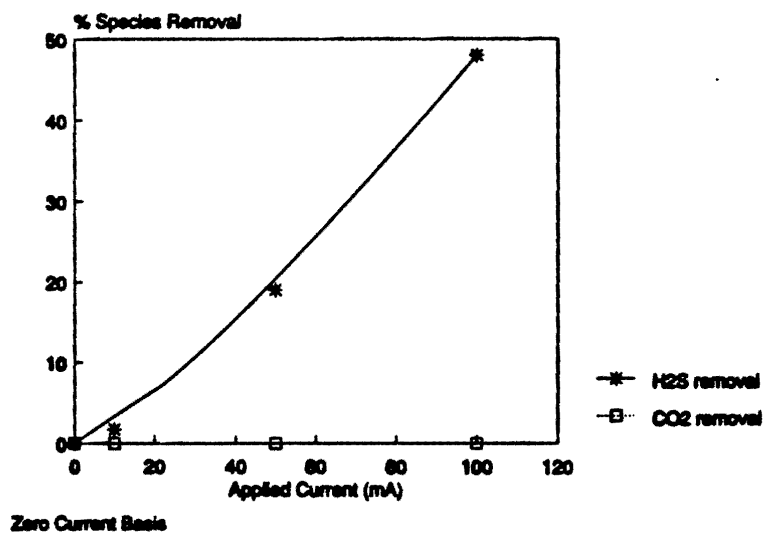
both nickel sulfide and nickel oxide species are conductive. Work will also continue on constructing a membrane from completely tape cast materials.



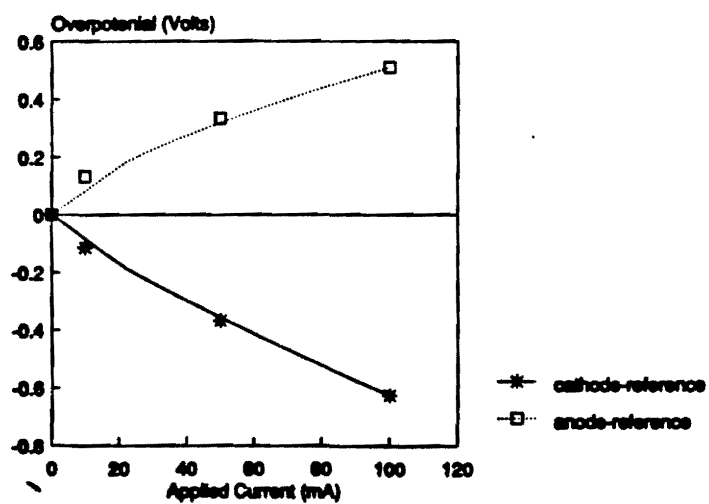
**Figure 7. Run 37: Species Removal vs Current**



**Figure 8. Run 37: Overpotential vs Current**



**Figure 9. Run 38: Species Removal vs Current**

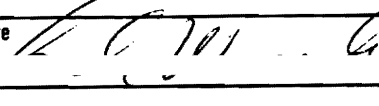


**Figure 10. Run 3 8: Overpotential vs Current**

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Quarterly Progress Report:  
High Temperature Membranes for  
 $\text{H}_2\text{S}$  and  $\text{SO}_2$  Separations  
Grant DE-FG22-90PC90293  
March 1, 1991 - June 30, 1991

by

Dr. Jack Winnick  
Georgia Institute of Technology  
School of Chemical Engineering  
Atlanta, Georgia 30332-0100

## **Purpose and Goals of Research**

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  cell and the  $\text{SO}_2$  cell require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.

### **I. $\text{SO}_2$ Removal Cell**

#### **Introduction**

The key to successful application of this technique is the development of a membrane capable of supporting a current density of  $50 \text{ mA/cm}^2$  at total voltages near 1 Volt. Flooding of electrode pores by electrolyte has been identified as a problem, leading to increased polarizations over time. To reduce flooding, new materials and fabrication methods will be investigated to produce an homogeneous, theoretically dense membrane. The matrix material must have the proper particle size distribution to develop sufficient capillary forces to prevent the electrodes from withdrawing the electrolyte.



Three techniques will be used for construction of the membranes or 'tiles'. The first is 'hot-pressing' in which powders of matrix material and electrolyte are intimately mixed in a dry atmosphere. The second technique will involve manufacturing a sintered ceramic matrix without electrolyte present and then 'wicking' the molten electrolyte into the matrix voids by capillary action. In the third method, tape-casting, the matrix material, dispersed along with an organic binder in a liquid, is continuously formed into a dried tape on a substrate, maintained at constant thickness by an overhead doctor blade. The flexible, 'green' tape is cut to the desired size, the binder is burned out, and the matrix is sintered, leaving a rigid body of the porosity needed for the final tile. Electrolyte is then infiltrated at operating temperature.

## **Research Summary**

Work during the quarter concentrated on a final determination of suitability for the commercial Ni electrodes oxidized in situ and several full cell tests using different electrodes and ceramic loading in the membranes. Full cell tests showed the ERC electrodes to flood, impeding removal rates. These electrodes have since been discarded for a different commercially available electrode (National Standard Fibrex mesh).

### **A. Electrodes**

Following up on last quarter's report, the National Standard Fibrex nickel electrodes were analyzed with X-ray powder diffraction to confirm the phases present after oxidation and exposure to electrolyte. After oxidizing the Ni electrodes in air at

600° C for 24 hours, the only NiO (Bunsenite) was observed. A piece of lithiated NiO was treated in  $K_2S_2O_7$  for 24 hours to determine chemical stability. The major phases were  $LiNiO_2$  and NiO, with some  $K_2Ni_2(SO_4)_3$ . The  $K_2Ni_2(SO_4)_3$  is a reaction product, most likely caused by reaction with exposed Ni on the surface. When the NiO is formed, the material goes through a 19% volume expansion (119% original size). Since the metal and the oxide have different thermal expansions, it is possible that cracks form in the oxide surface upon cooling, creating bare Ni surfaces prone to attack by  $K_2S_2O_7$ . As mentioned in the last quarterly report, no degradation was seen during full cell tests. Full cell tests during the present quarter have confirmed this to be the case. The formation of nickel sulfates may be prevented by the thorough lithiation and oxidation of the electrodes and will be studied in the coming quarter.

Additional Ni electrodes were obtained from Energy Research Corporation (ERC). This proprietary material was lithiated and oxidized, at different temperatures, to determine the effect of oxidation temperature on room temperature conductivity. At the lower temperatures, the surface exposed to air was darker than the underside, showing a possible limitation towards oxidation. All samples warped, due to either residual stress relief during heating or a loss of ductility in the oxidized area. The room temperature resistances are tabulated below and show a strong dependence on firing temperature. All electrodes used in full cell tests were prepared at 575° C. Scanning Electron Microscopy will be performed in the next quarter to determine the pore sizes of these electrodes.

Firing Temperature, and Time	Upper Surface Resistance (Room T)	Lower Surface Resistance (Room T)
500° C; 24 hrs.	220 $\Omega$	1770 $\Omega$
550° C; 12 hrs.	145 $\Omega$	600 $\Omega$
600° C; 2 hrs.	5 - 10 $\Omega$	4 - 10 $\Omega$
600° C; 2 hrs.	7 - 16 $\Omega$	1.4 - 3 $\Omega$

## B. Tape Cast Membranes

Some difficulties were encountered making tapes, due to the increased humidity of the summer months. Previous membrane formulations stuck to the substrate. These substrates of polyethylene terephthalate and glass, whether coated with a release agent or not, were no longer suitable for tape casting. The replacement, galvanized steel sheet, requires no release agent. Also, tapes with higher ceramic loadings ( > 45 vol. %) had small mud cracks on the surface; this problem was overcome by slowing the drying rate.

Several different ceramic loadings were produced and tested in the cell, including 31, 42 and 50 volume percent ceramic ( $\text{Si}_3\text{N}_4$ ) in the Metoramic Sciences, Inc. vinyl butyral binder system (B73305). An added surfactant and sonication of the blend produced homogeneous tapes.

## C. Full Cell Tests

The first full cell test was conducted using ERC electrodes and a 31 vol. % ceramic tape cast membrane. The electrodes were cut to a size which would permit volume expansion to fill the electrode cavities upon oxidation. Due to the severe warping problem of the electrodes mentioned above, the electrodes were soaked in

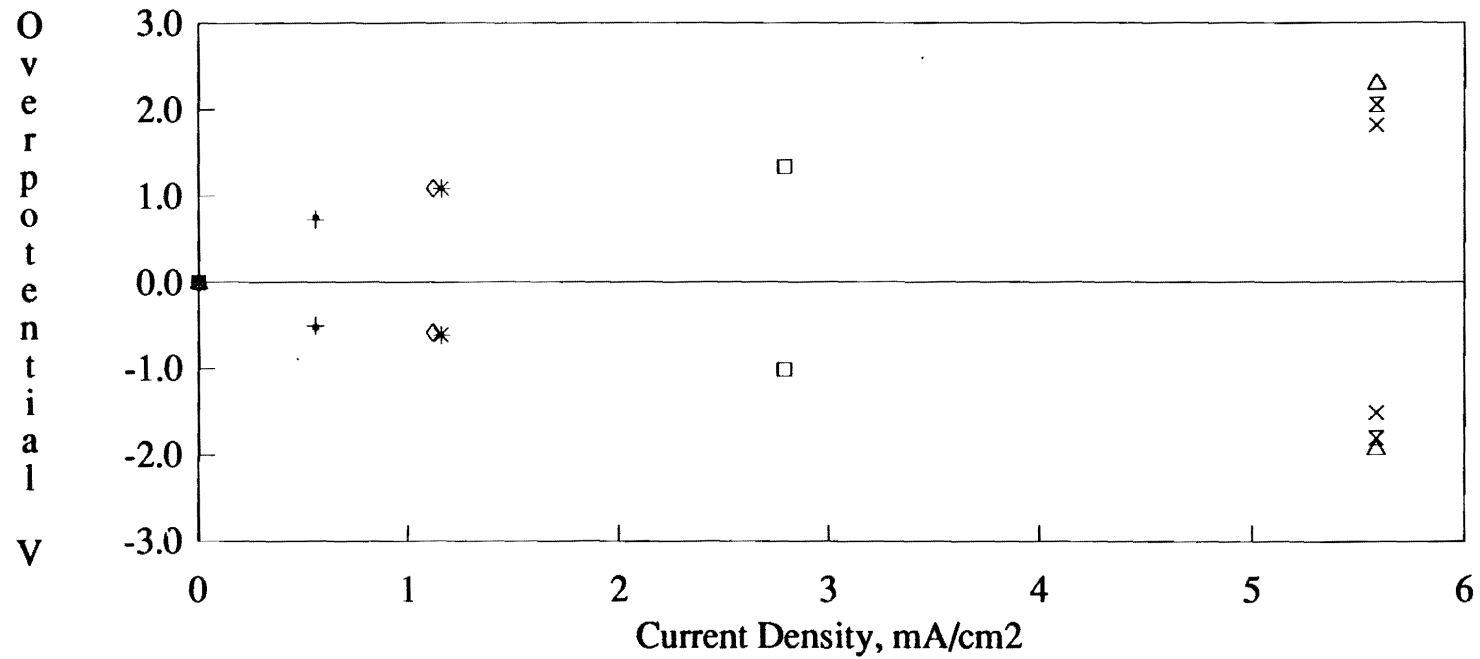
LiOH and dried, then placed in the cell housings along with the tape cast membrane. The components were then oxidized with pure  $O_2$  by slowly ramping to  $575^\circ C$  (the upper limit of the experiment furnace). An amount of electrolyte sufficient to fill the membrane voids was then added through the reference electrode port. Gas crossover, from one side of the membrane to the other, was immediately detected and could not be cured by additional electrolyte. Post-mortem analysis revealed the membrane to have cracked during binder burnout.

Since gas crossover was severe, this study focused on determining the effect of electrolyte level on polarization. The figures below show polarization curves for the different percentages of electrolyte at different times during the run. These percentages are based on calculated void volume in the tape after binder burnout. If more electrolyte is added than can be retained by the membranes and electrodes, it will run out of the cell. Excess electrolyte was detected in the gas channels and tubes, but could not be recovered for quantitative determination. Higher current densities were only achieved with the higher electrolyte loadings.

A major feature of these polarization curves is the apparent deviation of the polarization curve at higher current densities. The anodic and cathodic (positive and negative voltages) curves should be exponential, but instead show an increase in polarization at the highest current density. This behavior is characteristic of a gas phase mass-transfer limitation. This subject was investigated in the next run.

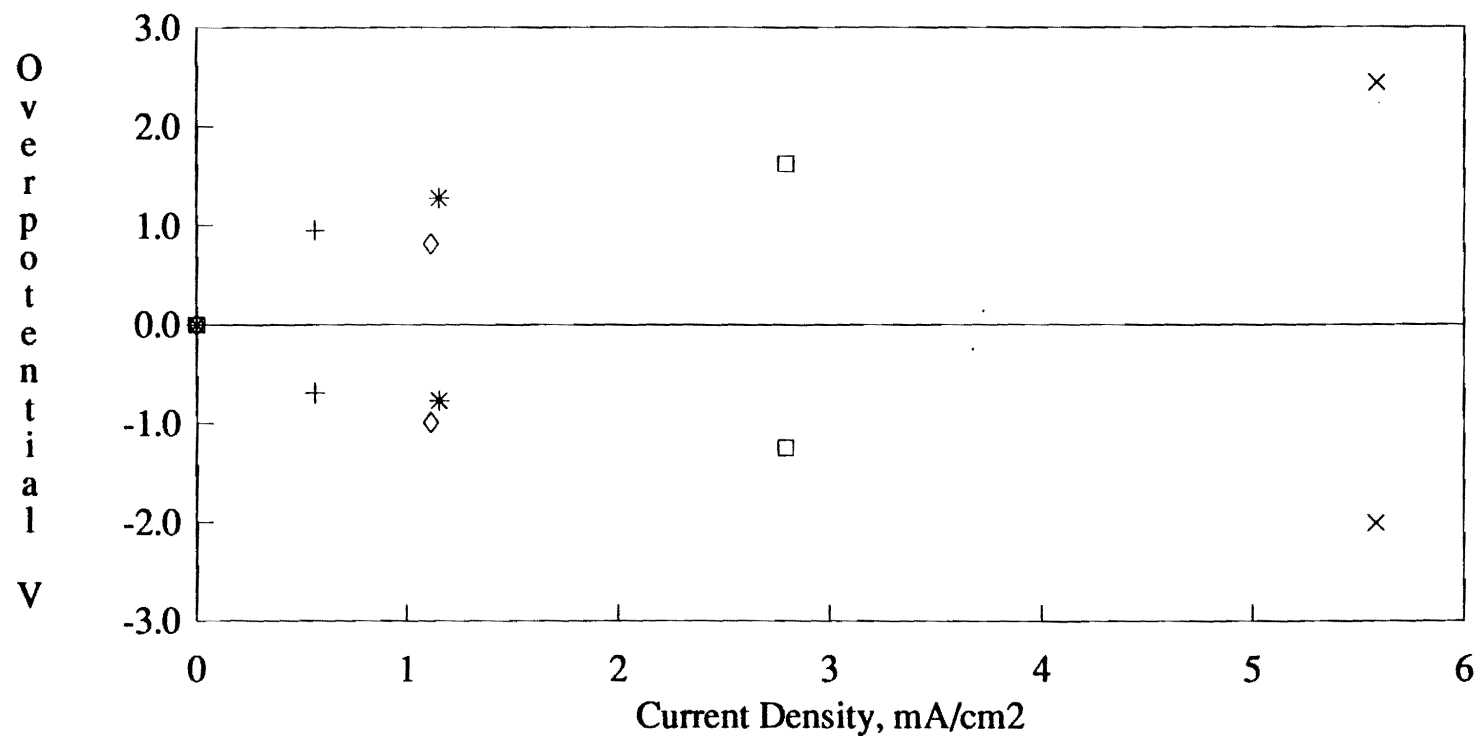
The second full cell test used the same electrode material and a 42 volume percent ceramic tape cast membrane. To prevent membrane cracking, the electrodes

# Overpotential with Varying Electrolyte Content (% Membrane Capacity)



Current on 10 mins

# Overpotential with Varying Electrolyte Content (% Membrane Capacity)



+ 118%   \* 140%   □ 163%   × 185%   ◇ 185%

Current on 60 mins

were oxidized before the membrane was added. The electrodes were again treated with a LiOH solution, dried and added to the electrode cavities. The cell was assembled with an alumina plate between the housings to prevent the electrodes from adhering to each other. Oxidation was achieved at 575° C in O<sub>2</sub> for 17 hours. The cell was then cooled and disassembled. The oxidized electrodes showed 12 - 22 Ω resistance from the lead wire to the electrode surface and 0.8 - 4 Ω resistance across each surface, well within requirements.

Two tape cast membranes were laminated at 1215 psi and room temperature to create a thicker membrane (0.9 mm thick) which would be less prone to cracking and gas crossover. At the same time, a thicker membrane creates a longer and more tortuous mass transfer path between the two electrodes, but this can be characterized by the resistance. The present membrane showed a low resistance at startup, proving the lamination to be effective. The SO<sub>2</sub> oxidation catalyst was added to the inlet tubes, the membrane was installed and the assembled cell was placed back in the oven. Binder burnout was achieved by slowly heating to 400° C in an O<sub>2</sub> atmosphere. When electrolyte was added, good seals were formed without gas crossover.

Polarization and removal studies were conducted in this full cell run. The initial application of 100 mA (90% stoichiometric removal current) showed only 16% removal of SO<sub>3</sub> at the cathode, no SO<sub>2</sub> generation at the cathode, and 76% generation of SO<sub>3</sub> at the anode. The second application of current (51.5 mA equals 90% stoichiometric removal) showed much greater removals at the start (93% SO<sub>3</sub> removal), then a gradual decay to 44% SO<sub>3</sub> removal. Generation of SO<sub>3</sub> at the anode

was less than stoichiometric (68%). The third application of current (100 mA equals 90% stoichiometric removal) showed even lower removals and excessive cathodic voltages. All of the above results lead to the conclusion that the ERC electrodes are flooding and reducing the available area for  $\text{SO}_x$  removal. This situation leads to an accumulation of sulfate at the interface, slowing the removal. Heating the cell from 400° C to 425° C caused the voltages to decrease in absolute value, a sign that residual sulfate melted and freed available surface area. This run was voluntarily terminated due to its poor performance.

Work begun in July, 1991 changed the electrode material from ERC electrodes to National Standard Fibrex mesh. These new electrodes have a more open structure, reducing the possibility of flooding. Some improvement has been seen and will be reported in the next quarterly report.



## II. H<sub>2</sub>S Removal Cell

### Introduction

This electrochemical removal cell cleans a product gas of H<sub>2</sub>S by electronating the most easily reduced component of the stream. In coal synthesis gas, this is H<sub>2</sub>S:



A membrane which contains sulfide ions in a molten state will act to transport sulfide across to the anode. If the membrane is capable of preventing diffusion of hydrogen from the cathode side, an inert sweep gas such as N<sub>2</sub> can be used at the anode to carry away oxidized sulfide ions as vaporous S<sub>2</sub>:

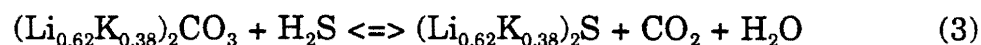


### Research Summary

Work has continued in the polishing applications of the electrochemical membrane separator with successful removal of H<sub>2</sub>S from 100 ppm down to below analytical limits of the gas chromatograph (approximately 2 ppm). Examination of the equilibrium composition of the electrolyte and membrane materials has also progressed with actual compositions being found to be close to predicted values for both the electrolyte and the electrode materials.

#### A. Electrolyte Analysis

The composition of the electrolyte present in the membrane of the cell reaches an equilibrium sulfide level based on the following reaction:



Theoretical compositions are calculated through an analysis of the Gibb's free energy of this reaction yielding the equilibrium constant by:

$$\ln K_a = - \Delta G/RT \quad (4)$$

with  $K_a$  defined as:

$$K_a = P_{CO_2} P_{H_2O} a_{M_2S} / P_{H_2S} a_{M_2CO_3} \quad (5)$$

If the activity coefficients of the molten phase constituents (namely the sulfide and carbonate in the electrolyte) are assumed to be unity, then equation (5) becomes:

$$K_a = P_{CO_2} P_{H_2O} X_{M_2S} / P_{H_2S} X_{M_2CO_3} \quad (6)$$

with  $X_{M_2S}$  and  $X_{M_2CO_3}$  defined as the mole fractions of sulfide and carbonate present in the melt such that:

$$X_{M_2S} + X_{M_2CO_3} = 1 \quad (7)$$

Actual compositions are measured by gravimetric analysis of total sulfur species present after oxidation with hydrogen peroxide. A sample of membrane material is weighed and then dissolved in water. The insoluble matrix materials are filtered and the filtrate is treated with excess hydrogen peroxide which oxidizes all sulfur species to sulfate. It is assumed that only sulfur in the form of sulfide is present in the membrane under run conditions. This solution is then acidified with hydrochloric acid to decompose the carbonate to carbon dioxide and water. The solution is boiled to de-gas the mixture and then barium chloride is added, causing the sulfate to precipitate as barium sulfate. The solution is then filtered, and the precipitate is rinsed, ignited, and weighed. The moles of barium sulfate precipitated is directly related to the moles of sulfide in the electrolyte.

Since the mass of the original sample is known, and the mass of the insolubles is known, then the mass of the soluble electrolyte present in the sample is known by difference. It is assumed that carbonate and sulfide species are the only components of the electrolyte, thus, the moles of carbonate is related to the moles of sulfide by equation (7). The results of this analysis are presented in Figure 1 for runs 37 through 40. Examination of this data shows that the equilibrium composition of the electrolyte can be closely approximated by the above analysis. The method is subject to a degree of experimental error, and this is shown in the variations between the theoretical and actual results. Still, the method does confirm the assumption of unity activity coefficients of the sulfide and carbonate species in the electrolyte melt. **B.**

## **B. Electrode Analysis**

Electrode analysis consists of three phases, solubles analysis, insolubles analysis, and bulk structure analysis. Each phase of the overall electrode analysis proceeds in the following manner.

### Solubles Analysis

This phase proceeds in a manner very similar to the technique outlined above for membrane electrolyte analysis. First, the electrode sample is ground and weighed. It is then washed in a water bath where the soluble components are dissolved. The soluble components consist primarily of electrolyte salts which have wicked into the pores of the electrode structure. There may also be some soluble electrode materials in the form of metal sulfates. Dissolved metal sulfates can be tested for by atomic absorption, and access to this test method is currently being

arranged. An attempt has also been made at determining the amount of dissolved metal sulfates by precipitation as metal hydroxides but the presence of barium and lithium in the final filtrate solution makes this method questionable as these metal hydroxide species are also insoluble. The results of this testing are discussed for each experimental run in the results section of this report.

#### Insolubles Analysis

This phase of electrode analysis is performed using x-ray diffraction. The results of this testing are discussed for each experimental run in the results section of this report.

#### Bulk Structure Analysis

This phase of electrode analysis is performed using scanning electron microscopy (SEM) techniques. The results of this testing are also discussed for each experimental run in the results section of this report.

### **C. Experimental Run Results**

#### Run 37

The composition of the electrolyte membrane from Run 37 (removal results discussed in the DOE report covering 1/1/91 to 4/1/91) was determined by the experimental methods described above. The final analysis showed the electrolyte to have a composition of 3.6 mole% sulfide and 96.4 mole % carbonate. An analysis of the equilibrium of reaction (1) shows a theoretical composition of 2.5 mole % sulfide

and 97.5 mole% carbonate (see Figure 1). The insolubles were found to be 67.5 wt%.

Initial results from a total sulfur species analysis on the electrolyte membrane yielded much higher sulfur levels than expected. However, it was found that sulfur from the electrode materials, which had adhered to the surface of the membrane, in the form of  $\text{CoSO}_4$  was adding significant error to the original experimental results. By driving the pH of the filtrate up with NaOH, dissolved Co was precipitated as  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . By subtracting the moles of Co precipitated from the total moles of sulfur present in the solution, the mole of sulfur present in the electrolyte could be found (one mole of dissolved Co translates to one mole of dissolved  $\text{CoSO}_4$  from the electrode materials).

### Run 38

An analysis of the membrane electrolyte from this run (removal results discussed in the DOE report covering 1/1/91 to 4/1/91) showed a sulfide level of 52.2 mole% and a carbonate level of 47.8 mole% (see Figure 1) with 58.2 wt% insolubles. This compares with theoretical values of 45.7 mole% sulfide and 54.3 mole% carbonate (in equilibrium with 0.963%  $\text{CO}_2$ , 0.212%  $\text{H}_2\text{S}$ , and 3.2%  $\text{H}_2\text{O}$ ). As in run 37, dissolved  $\text{CoSO}_4$  was subtracted from the total sulfur results by precipitating Co from the filtrate.

The composition of the Co precipitate from runs 37 and 38 were verified by ashing to  $\text{Co}_2\text{O}_4$ . The Co precipitates (assumed to be  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) were taken and ashed at a temperature of 850° C. This resulted in a black-purple substance with a

recorded weight change which corresponded closely to the predicted change for  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  going to  $\text{Co}_2\text{O}_4$ .

### Run 39

This experimental run used a layered membrane structure identical to that used in run 38. This was three mats of ZYW-30A zirconia cloth layered with three tapes of MgO ceramic, present as a matrix densifier. The electrolyte was initially lithium/potassium carbonate eutectic and was layered into the membrane during set-up. Gas composition was initially 1.43%  $\text{CO}_2$ , 96 ppm  $\text{H}_2\text{S}$ , 3.2%  $\text{H}_2\text{O}$ , and the balance  $\text{CH}_4$ . Due to a blown fitting, the source tank was drained approximately 95 hours into the run. Gas of consisting of 110 ppm  $\text{H}_2\text{S}$ , 1.39%  $\text{CO}_2$ , 3.2%  $\text{H}_2\text{O}$ , balance  $\text{CH}_4$  was subsequently provided to the cell by diluting a 2194 ppm  $\text{H}_2\text{S}$ , 0.994%  $\text{CO}_2$ , balance  $\text{CH}_4$  gas mixture with a 1.46%  $\text{CO}_2$ , balance  $\text{CH}_4$  mixture.

Both the cathode and the anode in this experiment were lithiated Ni electrodes provided by ERC. The exact properties of these porous nickel electrodes are proprietary. The initial pure Ni electrodes were lithiated by soaking in 1M LiOH overnight.

$\text{H}_2\text{S}$  removals down to 4 ppm were recorded, but a puzzling effect of applied current was observed. After several hours with zero applied current to the cell, the scrubbing effect of the carbonate electrolyte going to its equilibrium sulfide level and the Ni cathode being converted to NiS slowed to the point that a low level of  $\text{H}_2\text{S}$  could be observed exiting the cell. When high current levels were applied to the cell

(200 mA), there was observed a drop in the CO<sub>2</sub> exit concentration. However, the H<sub>2</sub>S exit concentration did not immediately decrease as expected based on experimental results from runs 37 and 38, but actually increased. The following explanation of this effect is hypothesized: as CO<sub>2</sub> and H<sub>2</sub>O go to CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub> under applied current, the H<sub>2</sub> acts to reduce any NiS to Ni and H<sub>2</sub>S which actually drives the exit H<sub>2</sub>S concentration of the cathode side up. This effect should continue until a new equilibrium is established (all NiS going to Ni) and then the H<sub>2</sub>S level should drop with applied current. This hypothesis was not tested during the course of the experimental run as the current was not left applied to the cell for a sufficient period of time to reduce all the cathode material back to Ni and no low current data (< 10mA applied) was taken.

Post-mortem analysis of the membrane electrolyte showed an actual sulfide level of 4.3 mole% and a carbonate level of 95.7 mole % with 64.0 wt% insolubles present. Theoretical analysis predicted a sulfide level of 6.5 mole% and a carbonate level of 93.5 mole% (see Figure 1).

An analysis of the limiting current density was performed in the following manner. Assuming that electrode kinetics and pore diffusion are rapid, membrane electrolyte transport was compared to gas phase transport. Using results from the electrolyte membrane analysis, the following equation describes the limiting current density through the membrane:

$$i_d = 2FD\rho\Delta C/\Delta x \quad (8)$$

where  $F = 96500$  coulombs/equivalent (Faraday's Constant),  $D = 10^{-5}$  cm<sup>2</sup>/sec

(assumed electrolyte diffusivity),  $\rho = 8.43 \times 10^{-3}$  gmoles/cm<sup>3</sup> (electrolyte molar density as inferred from membrane structure),  $\Delta C = 0.043$  (sulfide concentration gradient between cathode side and anode side assuming equilibrium composition on the cathode side and zero concentration on the anode side), and  $\Delta x = 0.23$  cm (membrane thickness). This analysis results in a predicted limiting current density through the membrane of 30.4 mA/cm<sup>2</sup>.

The membrane limiting current density is compared to the limiting current density as specified by the rate of gas-phase transport of H<sub>2</sub>S to the membrane surface. This is described by equation (9):

$$i_d = 2Fk\rho(y_{in} - y_{out})/\ln(y_{in}/y_{out}) \quad (9)$$

with  $k = 12.9$  cm/sec (from flow channel geometry and mass transfer principles),  $\rho = 1.31 \times 10^{-4}$  gmoles/cm<sup>3</sup> (gas density),  $y_{in} = 1 \times 10^{-4}$  (cathode side inlet H<sub>2</sub>S mole fraction),  $y_{out} = 1 \times 10^{-5}$  (cathode side exit mole fraction). From these conditions, the gas phase limiting current density is calculated to be 1.3 mA/cm<sup>2</sup>. This analysis shows that in this experiment, transport was gas phase limited, not electrolyte-migration limited. This is important as the gas phase mass transport to the surface of the membrane can be controlled by proper design of the gas flow channels.

Accurate compositions of the electrode material solubles could not be obtained by quantitative chemical analysis as with the Co electrode materials from runs 37 and 38. This is because of the precipitation of Ba and Li in addition to Ni hydroxides upon adding NaOH to the electrolyte wash solution. If, however, it is assumed that the amount of electrode material dissolved was small compared to the amount of



electrolyte dissolved, then it was found that the cathode was 81.8% flooded and the anode was 86.1% flooded. These levels of flooding are high, indicating that most of the electrode pores were completely flooded. This limits the gas / electrolyte interface surface area and decreases the overall cell performance by decreasing the active interface area. A larger average pore size would give better results as the capillary forces drawing the electrolyte out of the membrane and into the electrode would be smaller.

An analysis of the insoluble components of the cathode by x-ray diffraction revealed four major phases. The largest proportion of material was NiO, Ni, and NiS with a smaller amount of Ni<sub>3</sub>S<sub>2</sub>. The presence of Ni, NiS, and Ni<sub>3</sub>S<sub>2</sub> were expected in the reducing environment of the cathode. The presence of NiO, however, was a surprise until the equilibrium of reaction (10) was examined.



$$K_a = P_{\text{H}_2}/P_{\text{H}_2\text{O}} \quad (11)$$

At run conditions, the equilibrium constant defined by equation (11) has a value of 0.0052. Since the H<sub>2</sub>O concentration was approximately three orders of magnitude higher than the concentration of H<sub>2</sub> in the cathode gas (>3% H<sub>2</sub>O compared to <100 ppm H<sub>2</sub>), reaction (8) was driven to the right. A comparison of the x-ray diffraction patterns for the cathode material with the characteristic diffraction patterns for the above mentioned materials is presented in Figure 2.

X-ray diffraction analysis of the anode material showed this electrode to be composed entirely of NiO. This is the expected phase in the oxidizing environment

of the anode. The x-ray diffraction pattern of the anode is compared to the diffraction pattern of NiO in Figure 3.

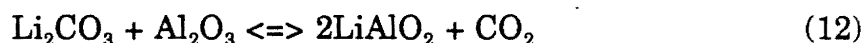
The bulk structure of the electrode materials was examined by Scanning Electron Microscopy (SEM) techniques. An example of an unused Ni electrode is presented in Figure 4. Since these electrodes were provided by ERC and are proprietary materials, the scale on the photographs has been hidden. However, for purposes of comparison, the magnification level on all photographs presented in this report are the same.

A photograph of the unwashed cathode material is presented in Figure 5. Note the crystals of frozen electrolyte lining the pore in the image. All surfaces appear to be coated with electrolyte. A photograph of the unwashed anode material is presented in Figure 6. In addition to a few crystals of frozen electrolyte, the pore surfaces appear to be coated with a poorly conducting material (evidenced by its light appearance against the highly conductive NiO material of the anode) which is thought to be condensed and solidified elemental sulfur. Since at run temperature the sulfur would be vaporous, this would have to be from sulfur vapor concentrated in the pores which condensed during cool down to ambient temperature.

#### Run 40

This experimental run used a layered membrane structure similar to that used by run 39, except that the layers of ZYW-30A were contacting the wet seal areas instead of MgO tape. Aluminum foil gaskets were also cut and laid into the wet seal

area between the membrane and the MACOR housings. This was done in an attempt to improve the wet seal of the cell by intimately binding the membrane structure to the MACOR housings with a layer of  $\text{LiAlO}_2$  formed in-situ. During heat-up to run temperature, the aluminum was converted to  $\text{Al}_2\text{O}_3$  and then to  $\text{LiAlO}_2$  through a subsequent reaction with  $\text{Li}_2\text{CO}_3$ :



This run used carbon at the cathode and Ni (converted to NiO in-situ) at the anode. The choice of carbon was made in an attempt to isolate electrochemical  $\text{H}_2\text{S}$  removal by working around the "sulfide sink" presented by allowing an Ni electrode form metal sulfide species in-situ. The process gas for this run had a composition of 98 ppm  $\text{H}_2\text{S}$ , 1.45%  $\text{CO}_2$ , 3.9%  $\text{H}_2\text{O}$ .

Initially, cell seals were excellent. No cell cross-flow was detected and the cell was capable of pushing several inches of water back pressure. However, approximately 23 hours into the run a malfunction in the temperature controller allowed the cell to cool off to room temperature.  $\text{N}_2$  was started to both cathode and anode sides of the cell as soon as the fault was detected and the controller was repaired. Unfortunately, the membrane was slightly damaged during the cool-down from run temperature. The  $\text{LiAlO}_2$  gaskets lost integrity and began to leak. Cathode side to anode side bulk cross-flow was also detected. Current collector / electrode / membrane contact was also damaged as cross-cell resistances went from  $0.9\Omega$  to  $4.0\Omega$ . The cell would still pass current however, and cross-flow could be limited to cathode to anode side flow by decreasing the anode sweep flow rate.  $\text{H}_2\text{S}$  levels in the process

gas were brought as low as 2 ppm (below GC analytical limits) over the course of the run with application of as little as 5 mA (cathode flow rate = 450 cc/min) with cross-cell potentials of only around 0.8 volts and no detectable  $\text{CO}_2$  removal.

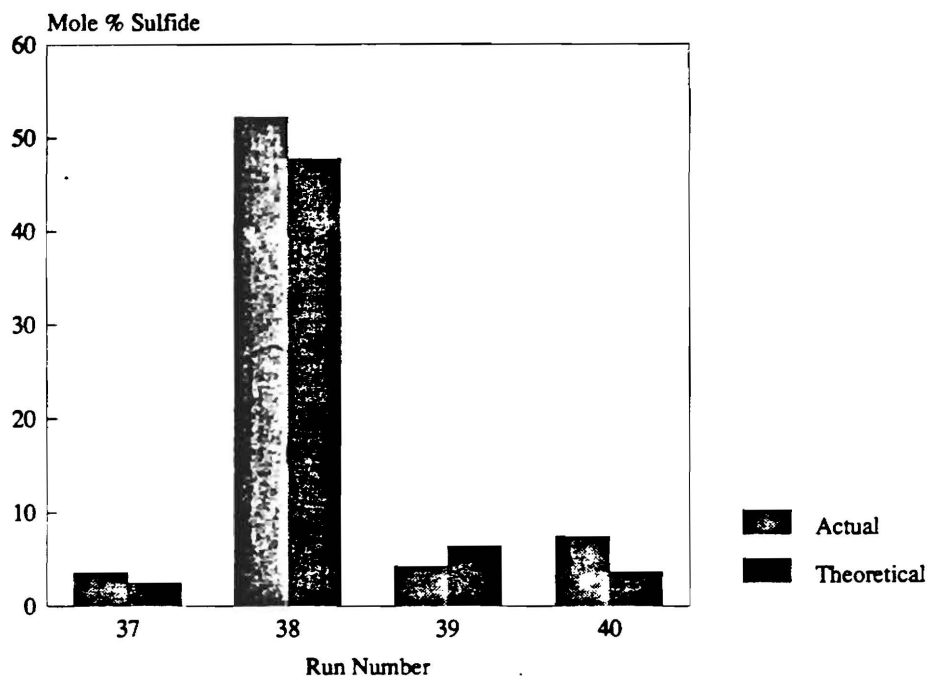
After 135 hours of operation, the cell was shut down for post-mortem analysis. The carbon cathode, while still operational, had degraded and was showing obvious signs of  $\text{H}_2\text{O}$  vapor erosion. The current collector on the anode side had also dissolved which explained the poor performance of the anode late in the run. A yellow tint was observed covering an area on the anode side wet seal where the seal had failed and was allowing sweep gas to be blown into the furnace. This tint could be sulfur, but analysis of the material has not yet been performed.

Post-mortem analysis of the membrane showed an actual sulfide level of 7.5 mole% and a carbonate level of 92.3 mole% with 60.1 wt% insolubles present. Theoretical analysis predicted a sulfide level of 3.7 mole% and a carbonate level of 96.3 mole% (see Figure 1).

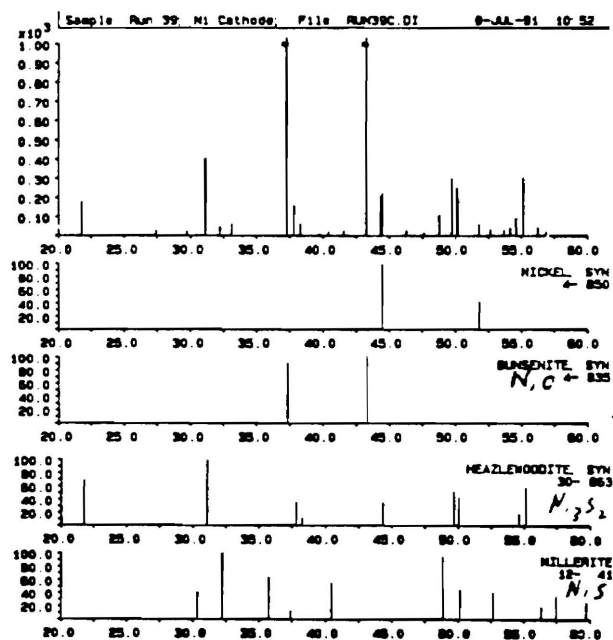
An analysis of the anode showed that the structure was only 62.9% flooded. The electrolyte which was wetting the pores of the electrode had an approximate composition of 4.8 mole% sulfide and 95.2 mole% carbonate. An analysis for dissolved  $\text{NiSO}_4$  was not performed. Examination of the x-ray data presented in Figure 7 shows that the primary insoluble species are Ni and NiO, as expected in this run environment. However, when the scale is decreased as in Figure 8,  $\text{Ni}_3\text{S}_2$  is seen to be present also. SEM examination of the electrode structure has not yet been performed.

#### **D. Future Work**

Work in this next quarter will continue in the polishing application of this technology with natural gas and coal synthesis gas systems. Cell structures identical to those used in Molten Carbonate Fuel Cell applications will be used as removal cells for polishing  $\text{H}_2\text{S}$  from simulated coal gasification streams. Studies of cathode and anode electrode material stability will also continue.



**Figure 1.**  
Electrolyte Composition (Actual vs Theoretical Sulfide)



**Figure 2.**  
X-Ray Diffraction Patterns, Cathode, Run 39

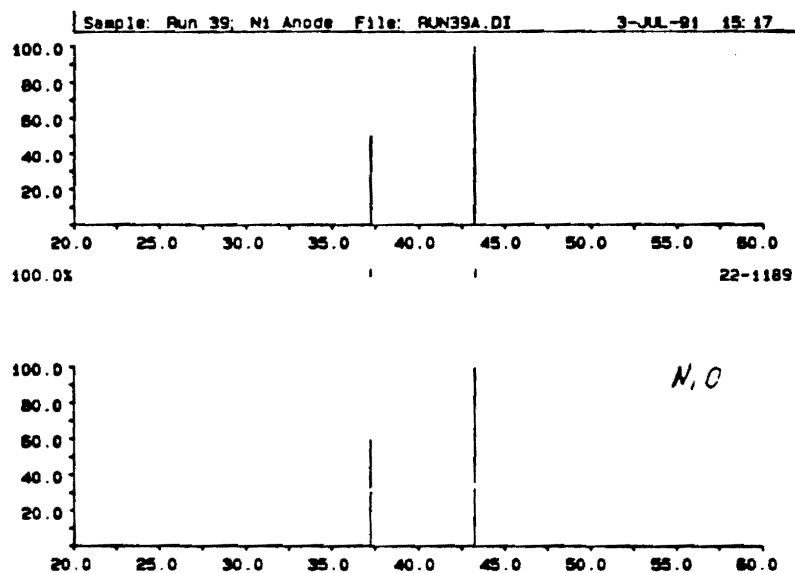


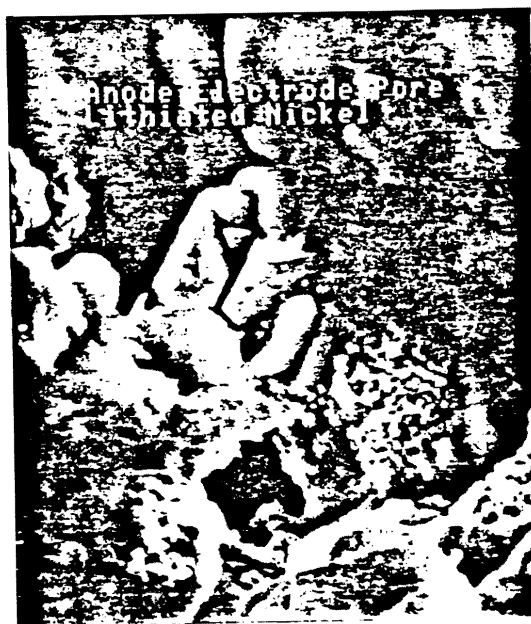
Figure 3.  
X-Ray Diffraction Patterns, Anode, Run 39



Figure 4.  
SEM Photograph, Unused Ni Electrode Structure



**Figure 5.**  
**SEM Photograph, Used Cathode Material, Run 39**



**Figure 6.**  
**SEM Photograph, Used Anode Material, Run 39**



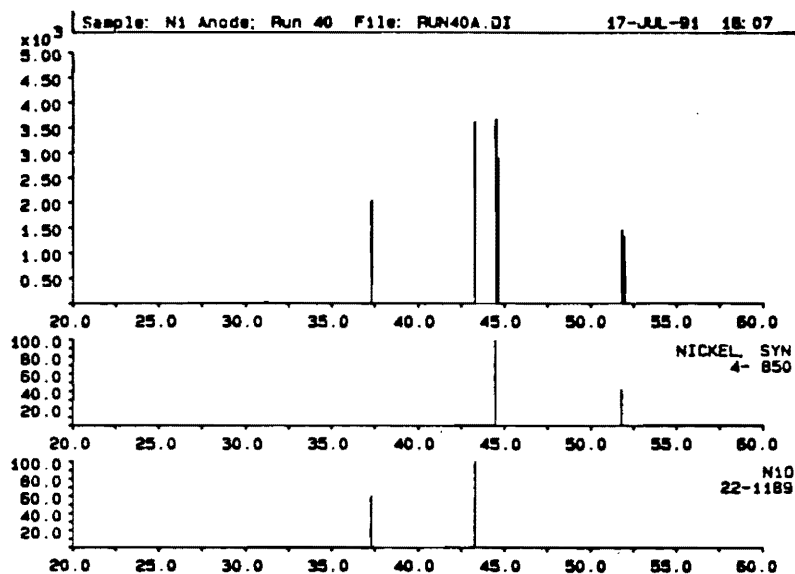


Figure 7.  
X-Ray Diffraction Patterns, Anode, Run 40

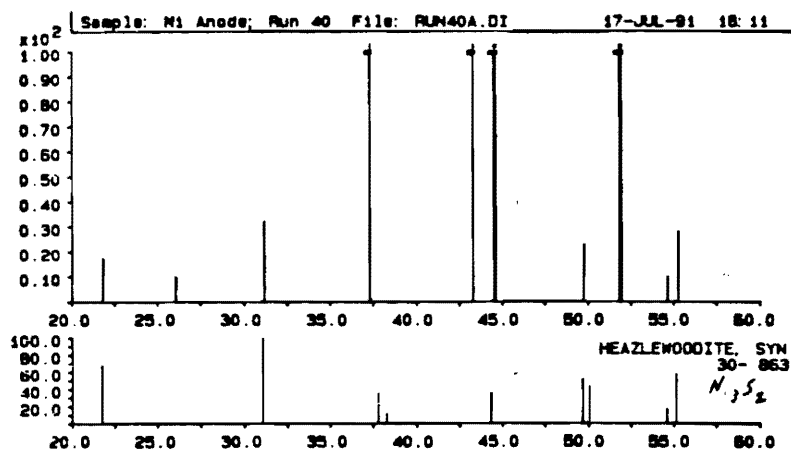


Figure 8.  
X-Ray Diffraction Pattern, Anode, Run 40 (Detail)

Quarterly Progress Report:  
High Temperature Membranes for  
SO<sub>2</sub> and H<sub>2</sub>S Separations  
Grant DE-FG22-90PC90293  
July 1, 1991 - September 30, 1991

by

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School of Chemical Engineering  
Atlanta, Georgia 30332-0100

## **Purpose and Goals of Research**

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  cell and the  $\text{SO}_2$  cell require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.

### **I. $\text{SO}_x$ Removal Cell**

#### **Introduction**

The key to successful application of this technique is the development of a membrane capable of supporting a current density of  $50 \text{ mA/cm}^2$  at total voltages near 1 Volt. Flooding of electrode pores by electrolyte has been identified as a problem, leading to increased polarizations over time. To reduce flooding, new materials and fabrication methods will be investigated to produce an homogeneous, theoretically dense membrane. The matrix material must have the proper particle size distribution to develop sufficient capillary forces to prevent the electrodes from withdrawing the electrolyte.

Three techniques will be used for construction of the membranes or 'tiles'. The first is 'hot-pressing' in which powders of matrix material and electrolyte are intimately mixed in a dry atmosphere. The second technique will involve manufacturing a sintered ceramic matrix without electrolyte present and then 'wicking' the molten electrolyte into the matrix voids by capillary action. In the third method, tape-casting, the matrix material, dispersed along with an organic binder in a liquid, is continuously formed into a dried tape on a substrate, maintained at constant thickness by an overhead doctor blade. The flexible, 'green' tape is cut to the desired size, the binder is burned out, and the matrix is sintered, leaving a rigid body of the porosity needed for the final tile. Electrolyte is then infiltrated at operating temperature.

## **Research Summary**

Work during the quarter concentrated on a final determination of suitability for the commercial Ni electrodes oxidized in situ and several full cell tests using different electrodes and ceramic loading in the membranes. Full cell tests showed the ERC electrodes to flood, which was confirmed via scanning electron microscopy. These electrodes have since been replaced by a different commercially available electrode (National Standard Fibrex mesh).

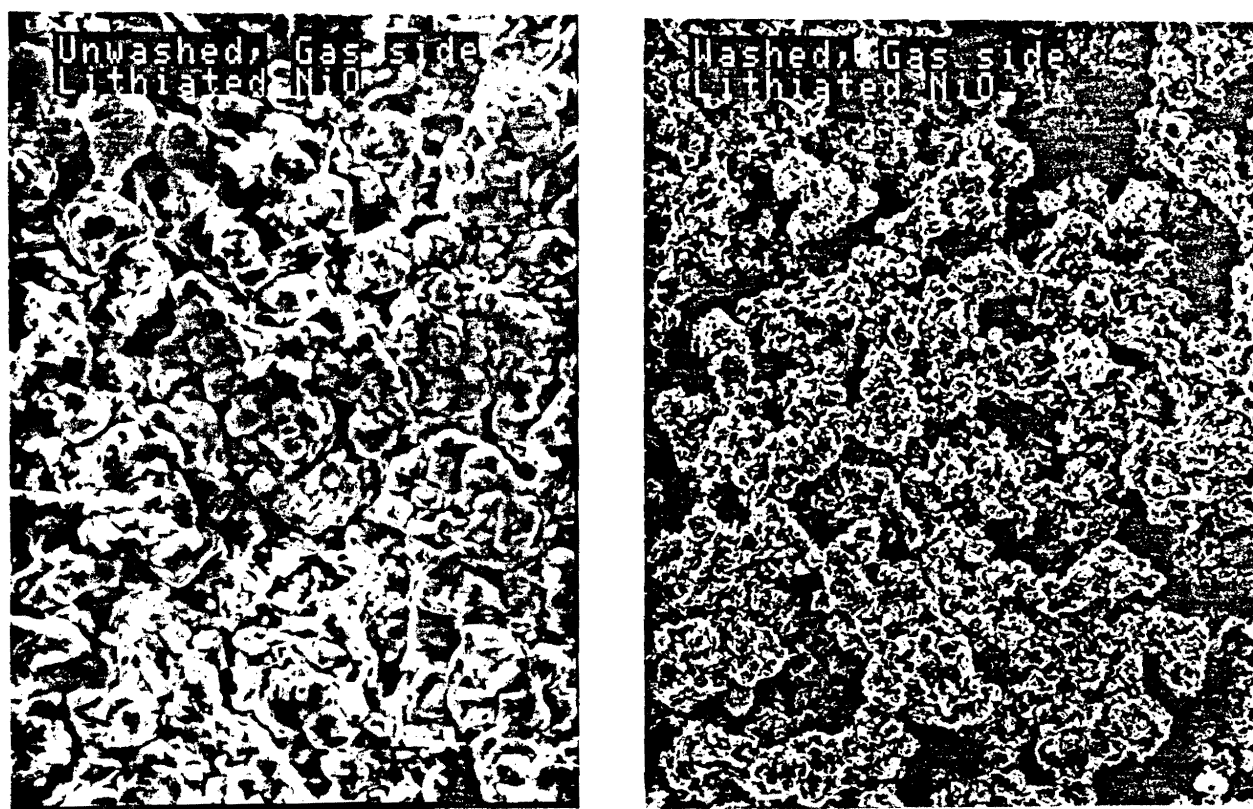
### **A. Electrodes**

#### **Electrode Characterization**

After electrode chemical stability tests proved successful last quarter, research progressed to characterize the surface and its interaction with the molten electrolyte.

Two electrode materials were studied; a proprietary nickel electrode from Energy Research Corporation (ERC) and a nickel mesh from National Standard (Fibrex).

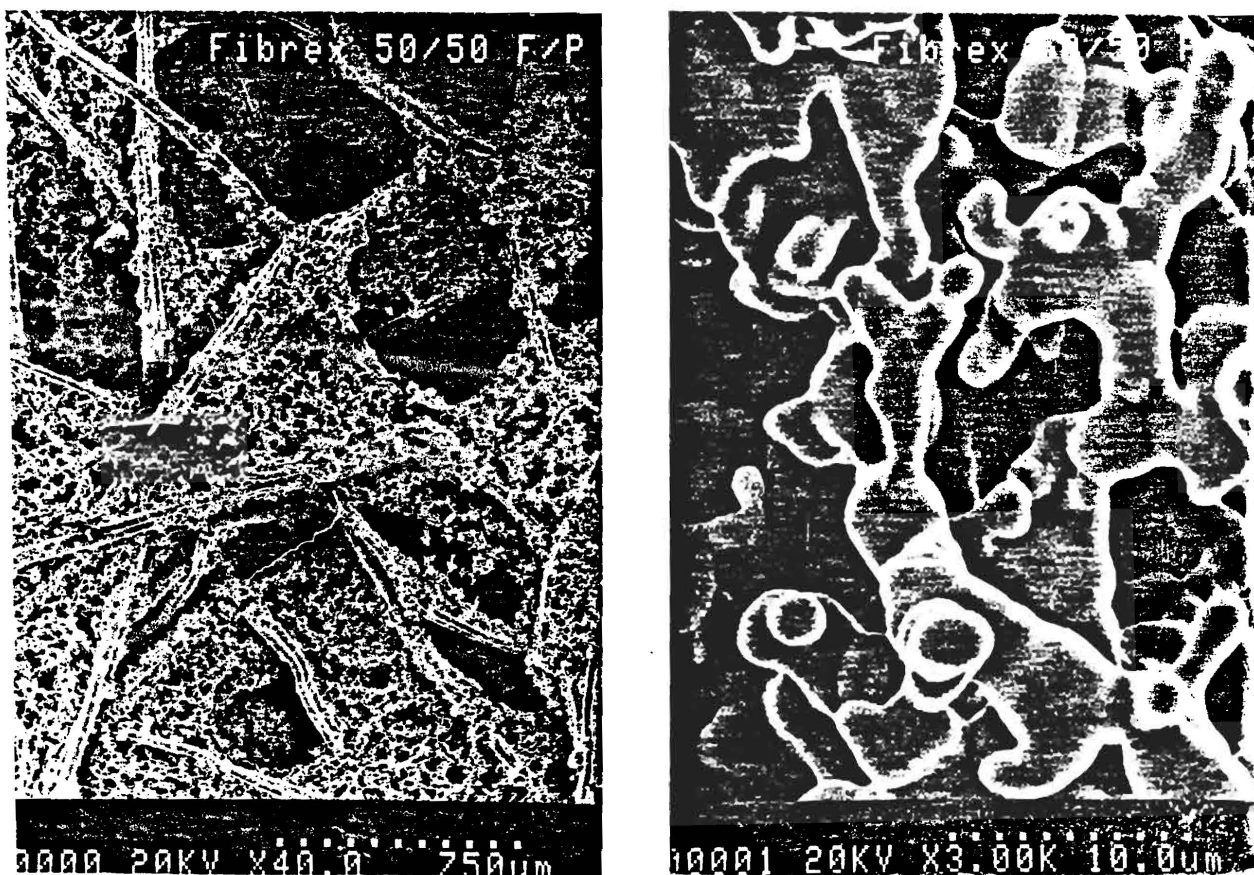
The ERC electrode is a sintered nickel body made from particle precursors, producing an electrode with small pores. Since this material is proprietary in nature, only the relative effects of electrolyte wetting will be discussed. Figure 1 shows two scanning electron micrographs of the electrode material after its use in a full cell study. The electrode material is in the lithiated and oxidized state. The micrograph on the left displays the surface exposed to gas after the cell was disassembled. The other micrograph exhibits the same surface after the electrolyte has been thoroughly



**Figure 1.** SEMs of ERC electrodes after use in the cell; unwashed (left) and washed (right). Both micrographs at same magnification.

washed away to expose the electrode. The effect of washing shows these electrodes to retain a large amount of electrolyte in the micropores, a symptom of electrode flooding. Many of the larger pores which run throughout the electrode are filled with electrolyte, reducing the surface area available for the removal of gaseous species. These SEMs confirm the behavior of the full cell during the run.

The Fibrex material is a sintered mesh of nickel fibers, each 25 microns nominal diameter, with powdered nickel carbonyl added to increase the structural strength of the bonds. The mesh is available in a variety of powder loadings, which has the effect of reducing the porosity of the mesh, while increasing the exposed surface area. Figure 2 displays two SEMs of the raw mesh (50% fiber, 50% powder

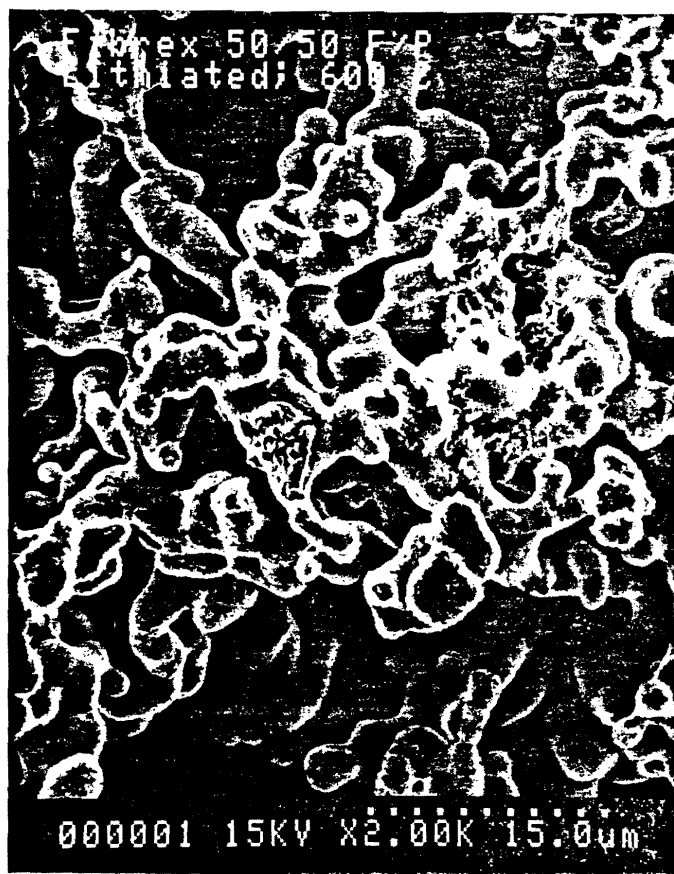


**Figure 2.** SEMs of Fibrex mesh, 50/50 : fiber/powder. Left, 40x; right, 3000x.

and 86% porous) at two different magnifications. The scan on the left, at 40x, shows the network of fibers with the powder covering the majority of the surface and providing an extensive network of macropores. The SEM on the right, at 3000x, provides a closer look at the micropores in the structure. The smooth nodules of nickel powder supply pores in the range of 1 to 10 microns, with very open gas flow passages between the micropores.

After treatment with LiOH, drying and subsequent oxidation of the Fibrex mesh, the surface of the nodules becomes coarse and the average pore size shrinks by about 20%. This shrinkage is caused by an expansion of the nickel as oxidation occurs (+19% volume change from Ni to NiO). Figure 3 shows the pores to range from 1 to 7 microns.

The SEMs served to characterize the pore structure of the electrode materials and allow us to determine which would suffer less flooding by



**Figure 3.** SEM of lithiated and oxidized 50/50 Fibrex Mesh.

the electrolyte during full cell studies. As confirmed in full cell tests to be described, the Fibrex electrode performs better in its contact with the electrolyte. Samples of the Fibrex electrode after use in the full cell will be examined in the next quarterly report.

## **B. Full Cell Studies**

Four full cell studies were conducted during this reporting period, with mixed results. One run provided very good polarization and  $\text{SO}_x$  removal data and is detailed in depth. The other runs suffered from electrical contact problems or gas leakage. All tape-cast membranes and electrodes were manufactured with the procedures discussed in the last quarterly report.

The first of the unsuccessful full cell studies suffered severe mechanical problems, such as broken glass gas feed tubes, no gas seal with the top housing and poor electrical contact between the lead wire and the electrode on the top half of the cell. With these problems, no practical polarization or removal data could be obtained. Post-mortem analysis showed the membrane to be firmly attached to the electrodes but not to the upper housing.

The successful run of the quarter was conducted with Fibrex electrodes and two 42 vol. % ceramic tapes laminated together. Superb seals were formed between the membrane and housings, but a decrease in sealing ability was noticed as the run progressed. Removal was quite high (>90%) and equivalent to stoichiometry, within the bounds of experimental error.

With applied current equal to 90% stoichiometric removal, cathodic removal of



$\text{SO}_3$  reached 90% or greater, given adequate time. Several levels of  $\text{V}_2\text{O}_5$  electrolyte loading were used, for reasons explained below. Figure 4 shows removal data after ten minutes of applied current. The data point at  $12.5 \text{ mA/cm}^2$  was obtained by following a different current path ( $5 \text{ mA/cm}^2 = 36\%$  removal for 2 hrs. then  $10 \text{ mA/cm}^2 = 72\%$  removal for 2 hrs.) which generated the required sulfate ions for high  $\text{SO}_3$  removal. Figure 5 shows removal data for the same runs, but after one hour. Removal is seen to be near 90%, in accordance with stoichiometry, for most currents, within the bounds of experimental error. Removal in excess of stoichiometry may be due to reaction with sulfate ions which have accumulated since current was applied, during the periods of lower removal, but is not outside the experimental error.

Looking at removal rates for 690 cc/min of cathode gas, excess removal above the stoichiometric level is seen for all applied currents in Figure 6. This is due to residual and excess sulfate in the electrolyte which is quickly neutralized by any  $\text{SO}_3$  present in the gas phase. The excess sulfate is caused by the generation of  $\text{SO}_2$  at the cathode (described next). Residual sulfate in the electrolyte from previous runs produces removal at zero current.

With the present configuration, a new phenomenon was observed. As current was applied,  $\text{SO}_2$  was seen to exit the cathode, Figure 7. This is possible from the electrochemistry of the system as seen by Scott<sup>1</sup> in free-electrolyte, but had not been observed before in high surface area (perovskite) electrode full cell tests. As current rises,  $\text{SO}_2$  is generated at a faster rate, one which overcomes the rate of oxidation by  $\text{V}_2\text{O}_5$  in the electrolyte. It appears that  $\text{SO}_2$  is diffusing out of the porous cathode

# SO<sub>3</sub> Removal

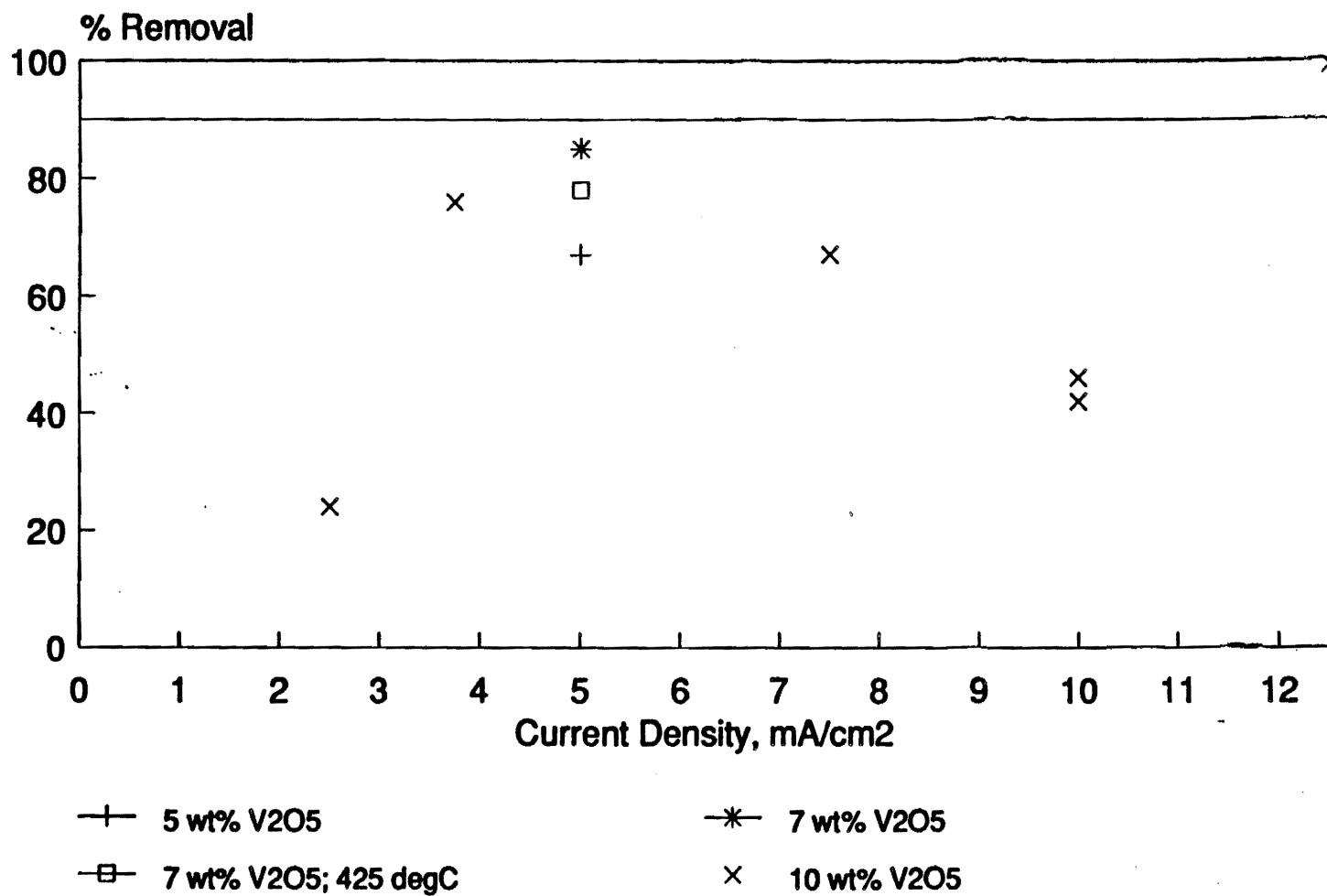
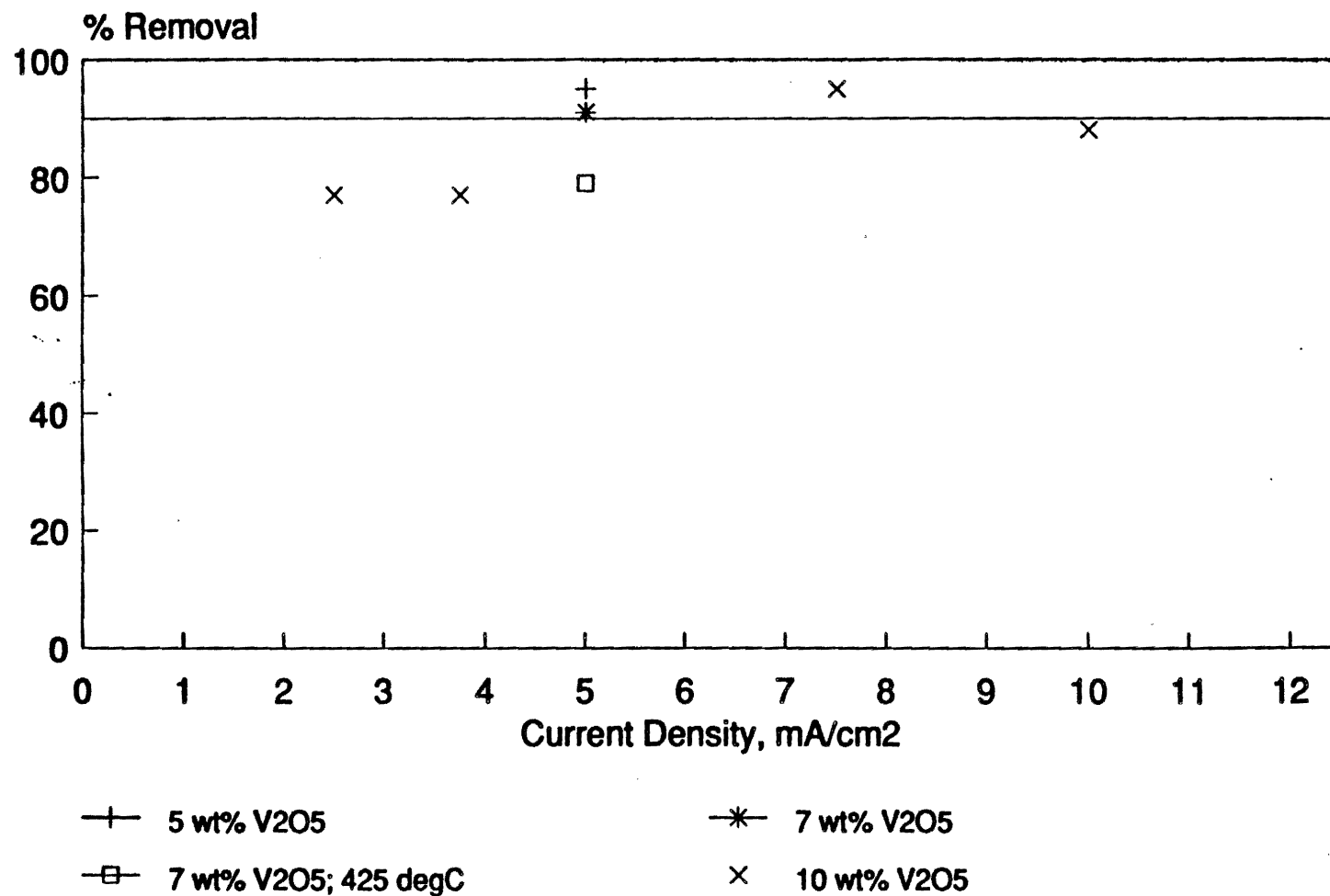


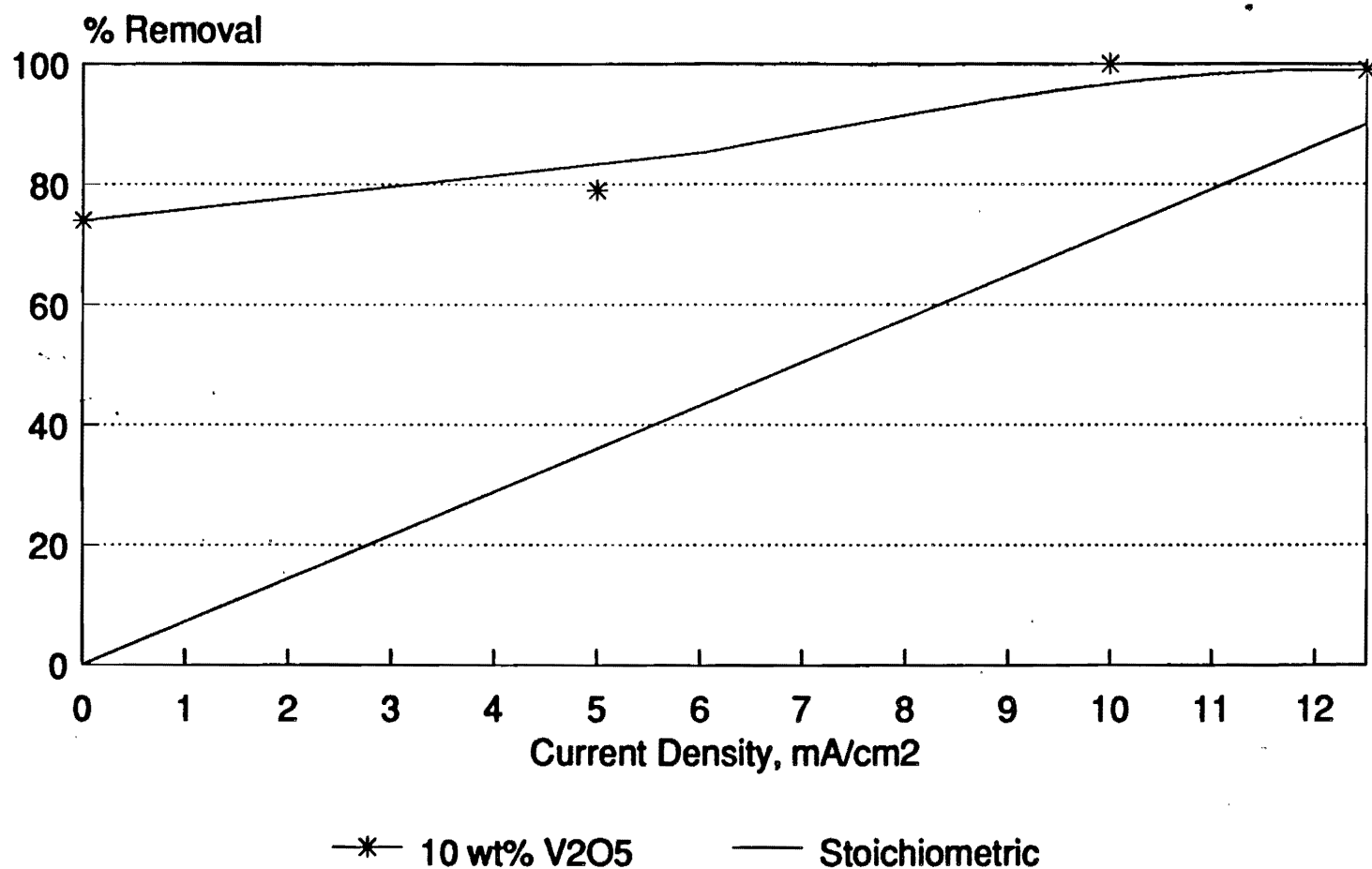
Figure 4. Cathodic removal of SO<sub>3</sub> after 10 minutes applied current. Flow of 0.3% SO<sub>2</sub>, 3% O<sub>2</sub> in N<sub>2</sub> equal to that required for 90% removal at applied current.

# SO<sub>3</sub> Removal



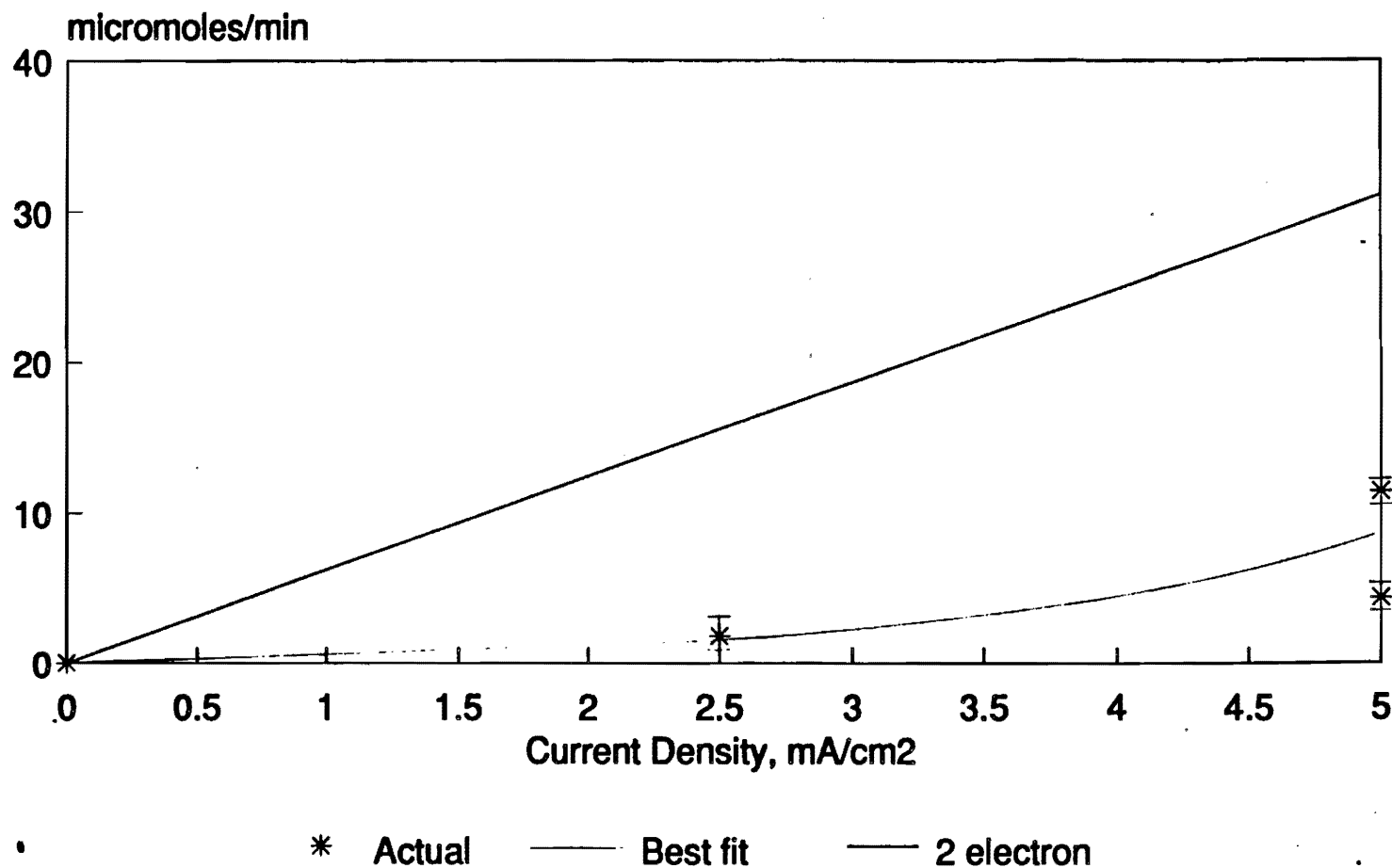
**Figure 5.** Cathodic removal of SO<sub>3</sub> after 60 minutes applied current. Flow of 0.3% SO<sub>2</sub>, 3% O<sub>2</sub> in N<sub>2</sub> equal to that required for 90% removal at applied current.

# SO<sub>3</sub> Removal



**Figure 6.** Cathodic removal of SO<sub>3</sub> with current. 690 cc/min of 0.31% SO<sub>2</sub>, 3% O<sub>2</sub> in N<sub>2</sub> fed to cathode. All inlet SO<sub>2</sub> oxidized to SO<sub>3</sub>. Line represents stoichiometric removal.

# Cathodic SO<sub>2</sub> Level 5 wt% V<sub>2</sub>O<sub>5</sub>



**Figure 7.** Cathodic SO<sub>2</sub> generation with applied current, with flow for 90% stoichiometric removal of inlet SO<sub>2</sub>. 5 wt.% V<sub>2</sub>O<sub>5</sub> in electrolyte.

before it can contact sufficient  $V_2O_5$  and is carried off by the passing gas stream. Calculations of outlet flow rates showed that one-half of the generated  $SO_2$  is being oxidized by the  $V_2O_5$  and removed at the cathode, for a 5 wt%  $V_2O_5$  electrolyte. To overcome this problem, more  $V_2O_5$  in  $K_2S_2O_7$  was added to the cell through the reference port. At 7 wt.%  $V_2O_5$  in the electrolyte, three-quarters of electrochemically generated  $SO_2$  was oxidized and removed, Figure 8.

At 10 wt.%  $V_2O_5$ , approximately 5/8 of generated  $SO_2$  was oxidized and removed according to calculation of the slope of the line through the data with applied current (Figure 9). This rate of oxidation is less than that for the 7 wt.%  $V_2O_5$  study, but two major differences were present. First, flow was continuously provided at a level such that 90% stoichiometric removal would occur at  $12.5 \text{ mA/cm}^2$ , so that  $SO_2$  which escapes the electrolyte at lower current densities does not have sufficient residence time to diffuse back to the electrolyte. Second,  $SO_2$  was present at zero current, showing that the pre-oxidation catalyst was not saturated with an equilibrium level of  $SO_2$  at the start of the run. Post-mortem analysis will confirm actual  $V_2O_5$  loading.

At the anode,  $SO_3$  generation is seen to deviate from stoichiometry at all  $V_2O_5$  levels, Figures 10 and 11. This discrepancy can be explained by two causes. The first, gas leakage out of the wet seal, accounts for most of the discrepancy at the higher  $V_2O_5$  and current levels. The second cause is attributed to residual sulfate ions accumulating at the anode, as seen by cathodic  $SO_2$  generation data. When  $SO_2$  is generated at the cathode and not oxidized and removed, excess sulfate ions accumulate in the electrolyte and migrate to the anode under the influence of the

# Cathodic SO<sub>2</sub> Level 7 wt% V<sub>2</sub>O<sub>5</sub>

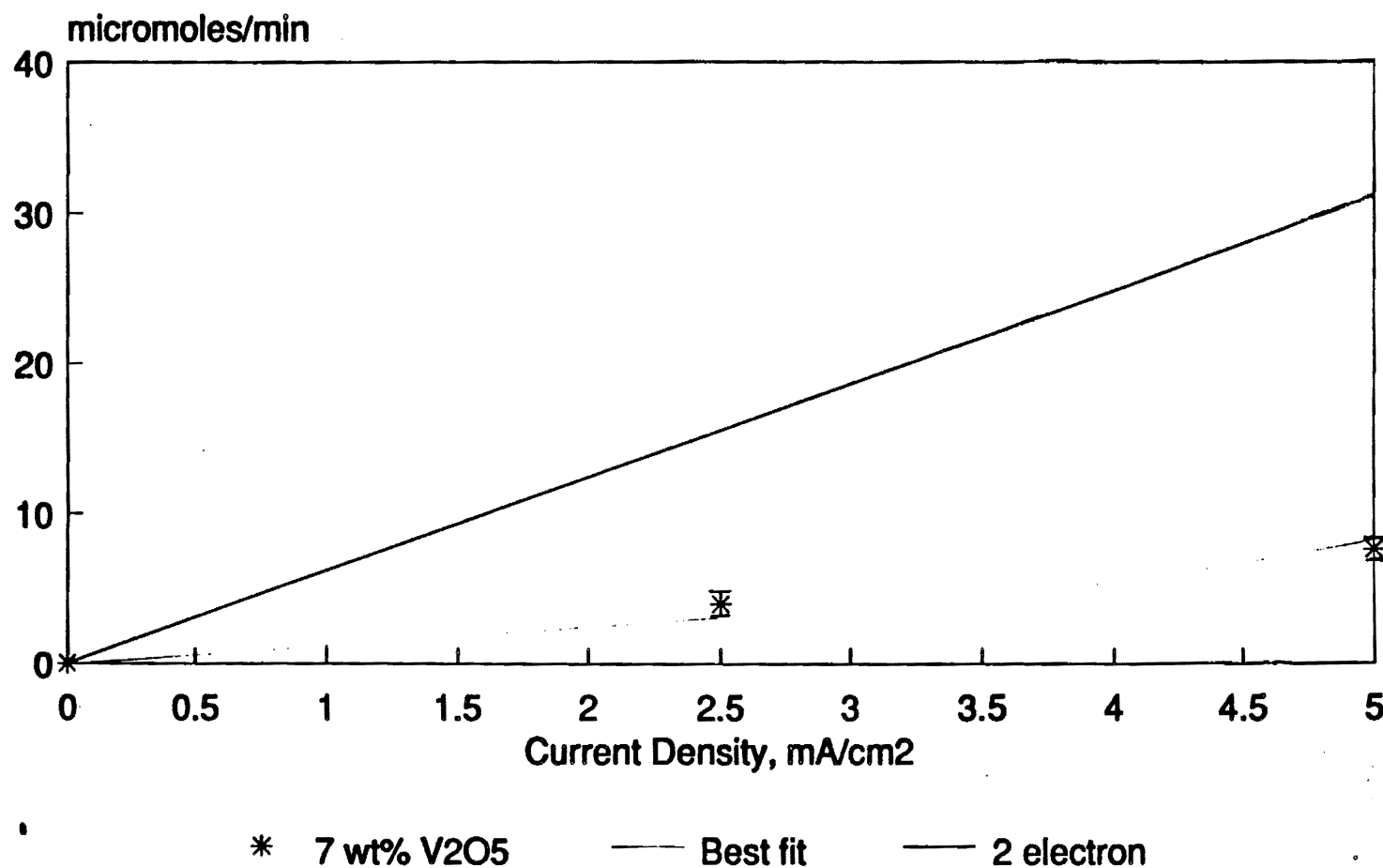
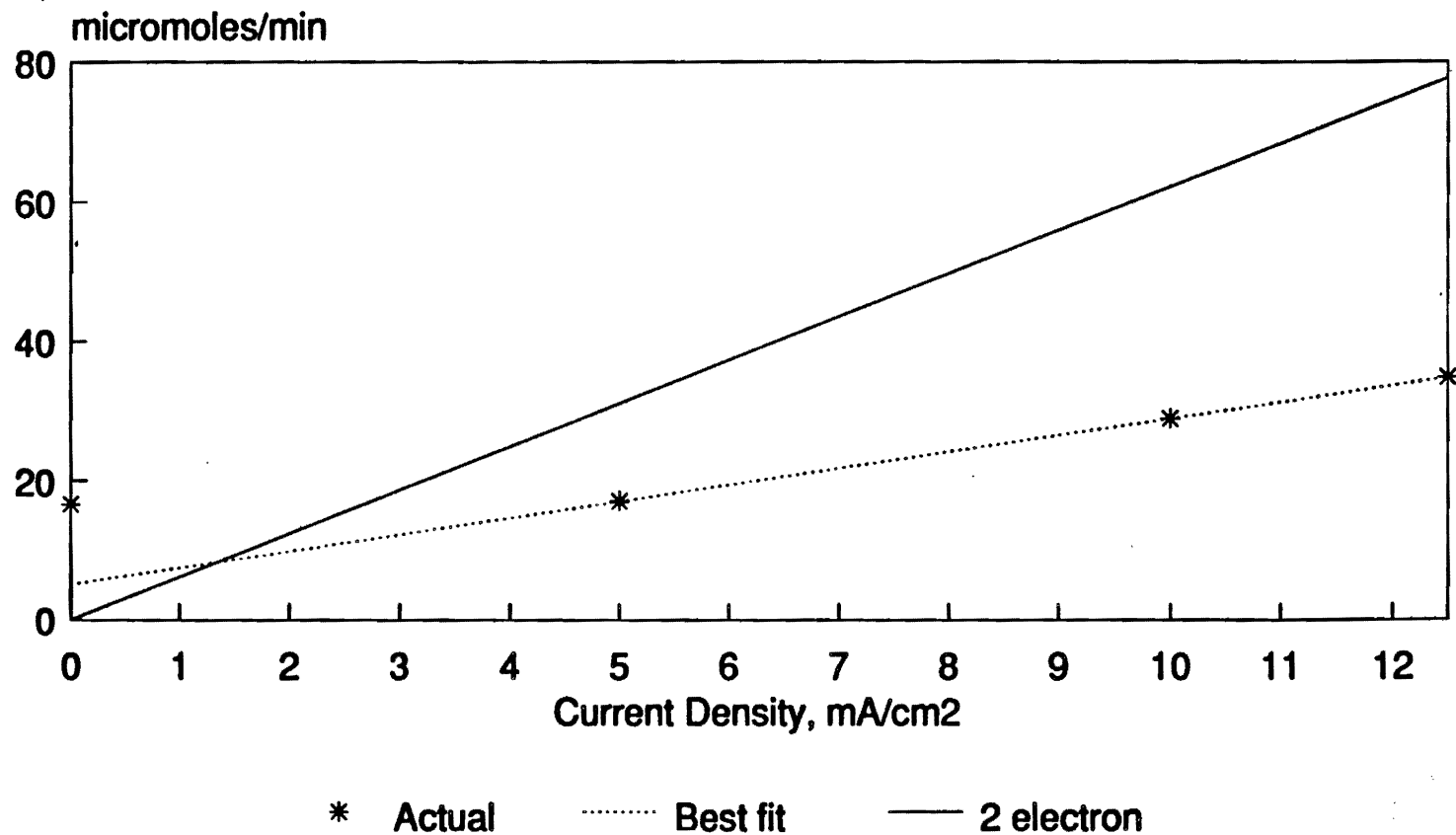


Figure 8. Cathodic SO<sub>2</sub> generation with applied current, with flow for 90% stoichiometric removal of inlet SO<sub>2</sub>. 7 wt.% V<sub>2</sub>O<sub>5</sub> in electrolyte.

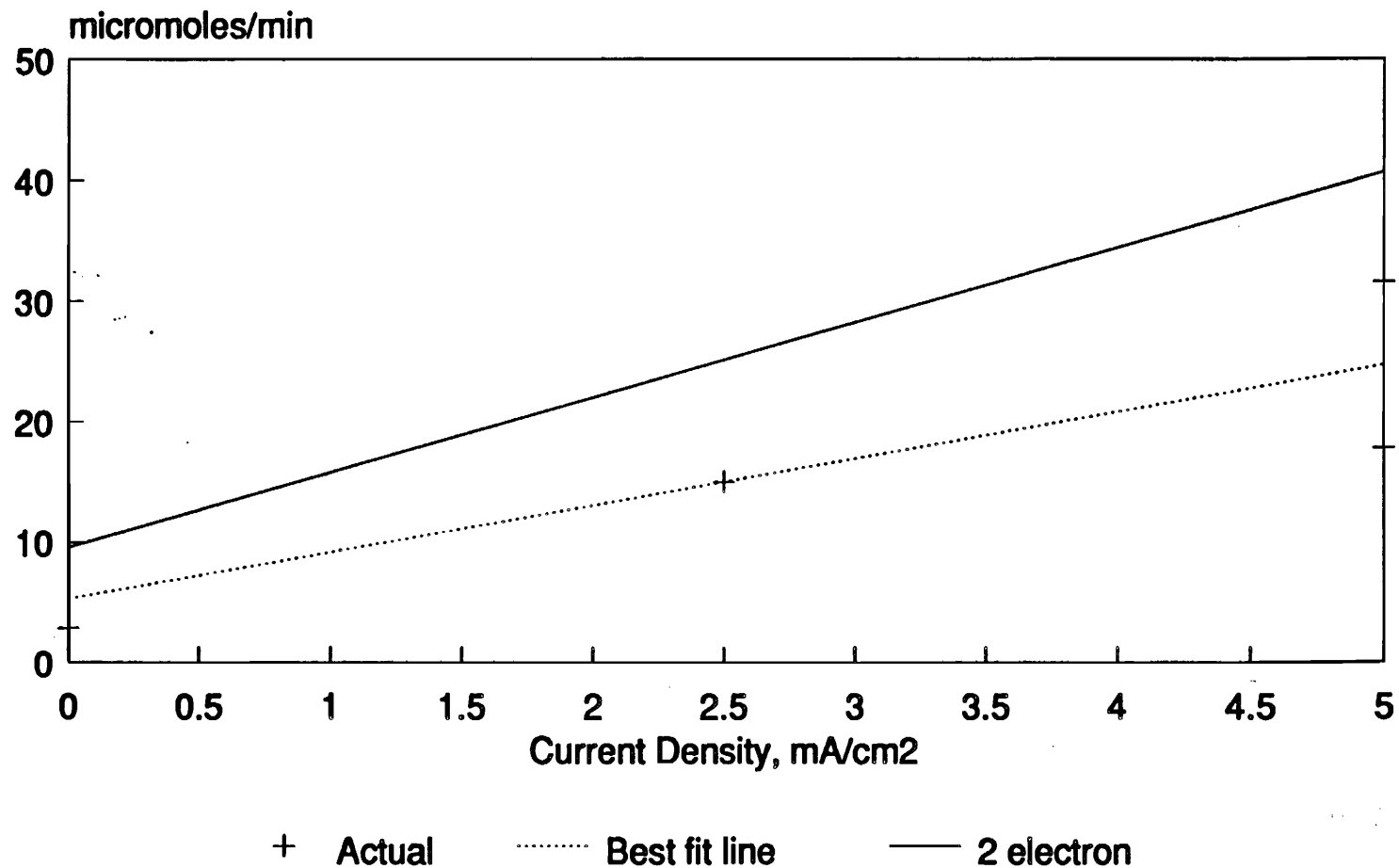
# Cathodic SO<sub>2</sub> Level 10 wt% V<sub>2</sub>O<sub>5</sub>



**Figure 9.** Cathodic SO<sub>2</sub> generation, with flow for 90% stoichiometric removal at 12.5 mA/cm<sup>2</sup>. 10 wt.% V<sub>2</sub>O<sub>5</sub> in electrolyte.



# Anodic SO<sub>3</sub> Flow Rate 5 wt% V<sub>2</sub>O<sub>5</sub>



**Figure 10.** Anodic SO<sub>3</sub> generation, 5 wt.% V<sub>2</sub>O<sub>5</sub> in electrolyte. Offset in calculated rates is due to oxidation of SO<sub>2</sub> fed to the anode side.

# Anodic SO<sub>3</sub> Flow Rate

## 10 wt% V<sub>2</sub>O<sub>5</sub>

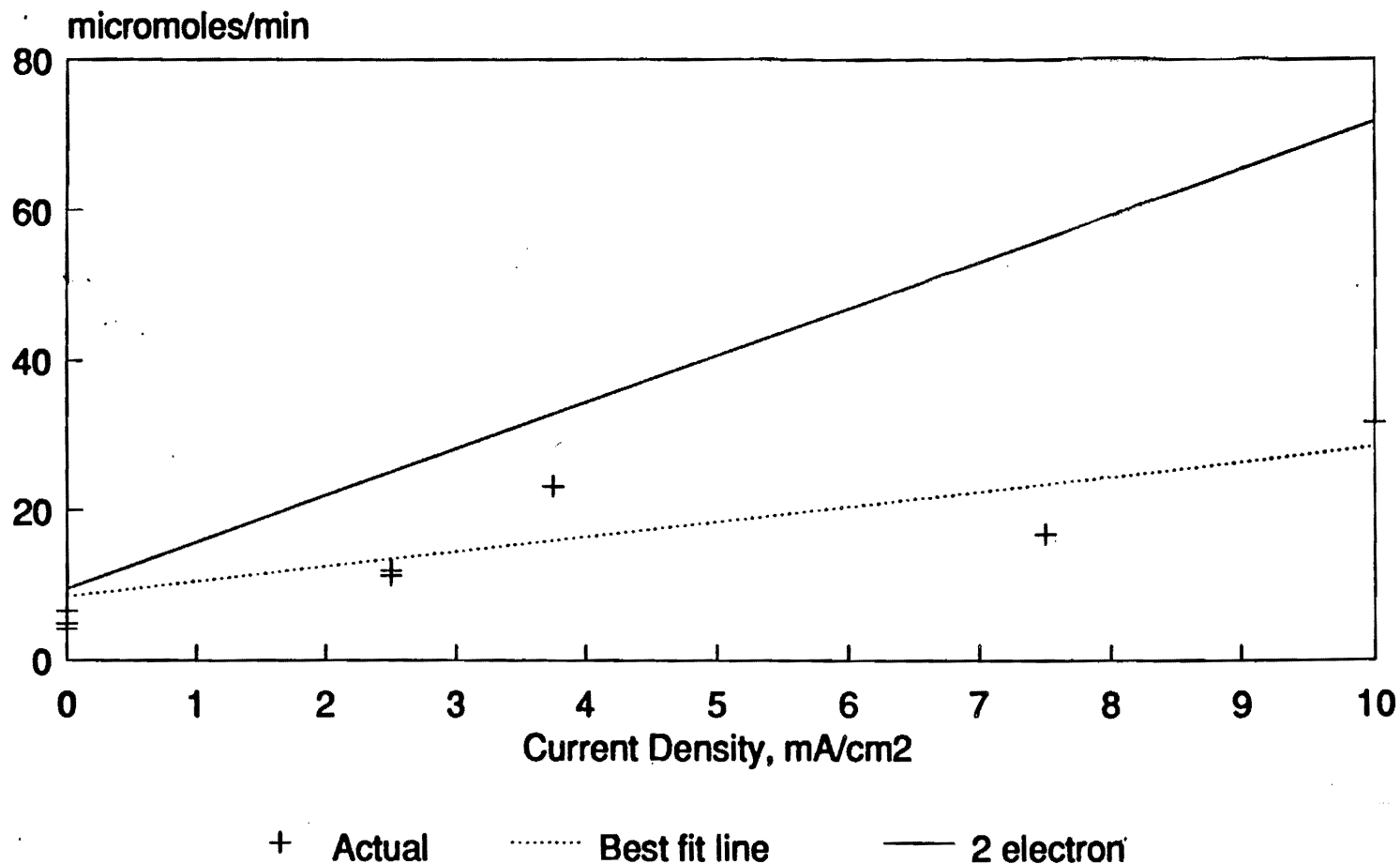


Figure 11. Anodic SO<sub>3</sub> generation, with 10 wt.% V<sub>2</sub>O<sub>5</sub> in electrolyte. Offset in calculated rates is due to oxidation of SO<sub>2</sub> fed to the anode.

applied electrical potential. Sulfate is either oxidized or raises the melting point of the electrolyte to the point where the electrolyte freezes on the anode surfaces. Excess sulfate at the anode will absorb electrochemically generated  $\text{SO}_3$  and neutralize it to form the  $\text{S}_2\text{O}_7^{2-}$  ion. This second phenomenon is confirmed by polarization data.

Polarization data for the full cell after 10 minutes of applied current are exhibited in Figure 12. The effect of increasing  $\text{V}_2\text{O}_5$  content is minimal after this short duration. After one hour of applied current (Figure 13), a greater effect of  $\text{V}_2\text{O}_5$  loading is observed. As  $\text{V}_2\text{O}_5$  content increases, polarization decreases. The anodic polarization suffers from sulfate accumulation at the lower  $\text{V}_2\text{O}_5$  loadings. This finding proves that increased vanadia loadings oxidize more of the cathodically-generated  $\text{SO}_2$  before it can escape from the electrolyte.

Also, as each current application progressed, the anodic overpotential and electrical resistance were seen to increase with time. This phenomenon confirms that accumulated sulfate migrates to the anode, where it raises the melting point of the electrolyte and retards the anodic electrochemical reaction. The increase in resistance shows that the sulfate is building up in the area of the electrical contact.

Electrochemical kinetic data can be obtained by properly treating the overpotential data. The Butler-Volmer equation of electrochemical kinetics,

$$i = i_0 [e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT}] \quad (1)$$

can be applied at low overpotentials in the linearized form of

$$i_0 = -\frac{RT}{nF} \left( \frac{di}{d\eta} \right) \quad (2)$$

# Polarization Varying V2O5 Content

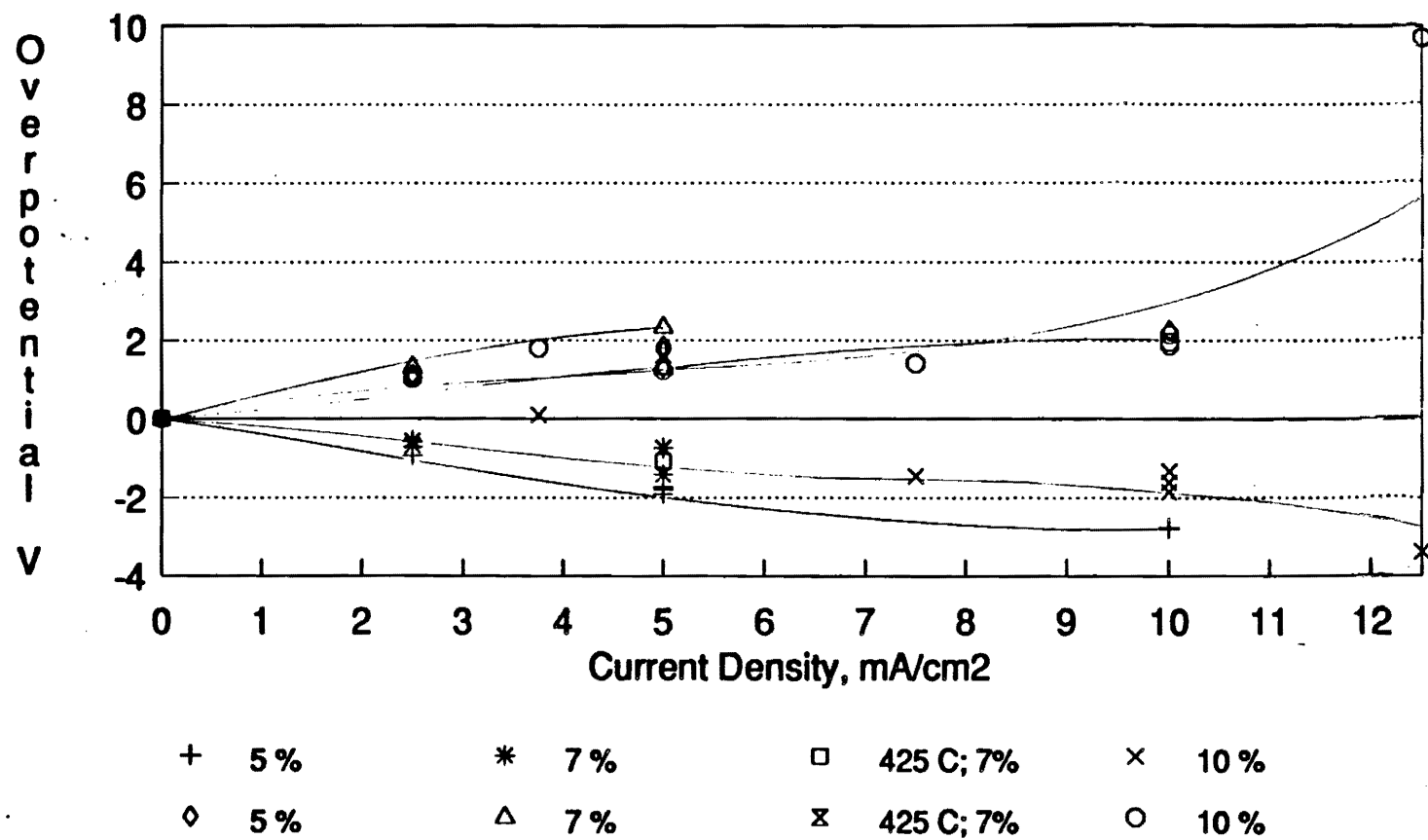


Figure 12. Polarization curves after 10 minutes of applied current.

# Polarization Varying V2O5 Content

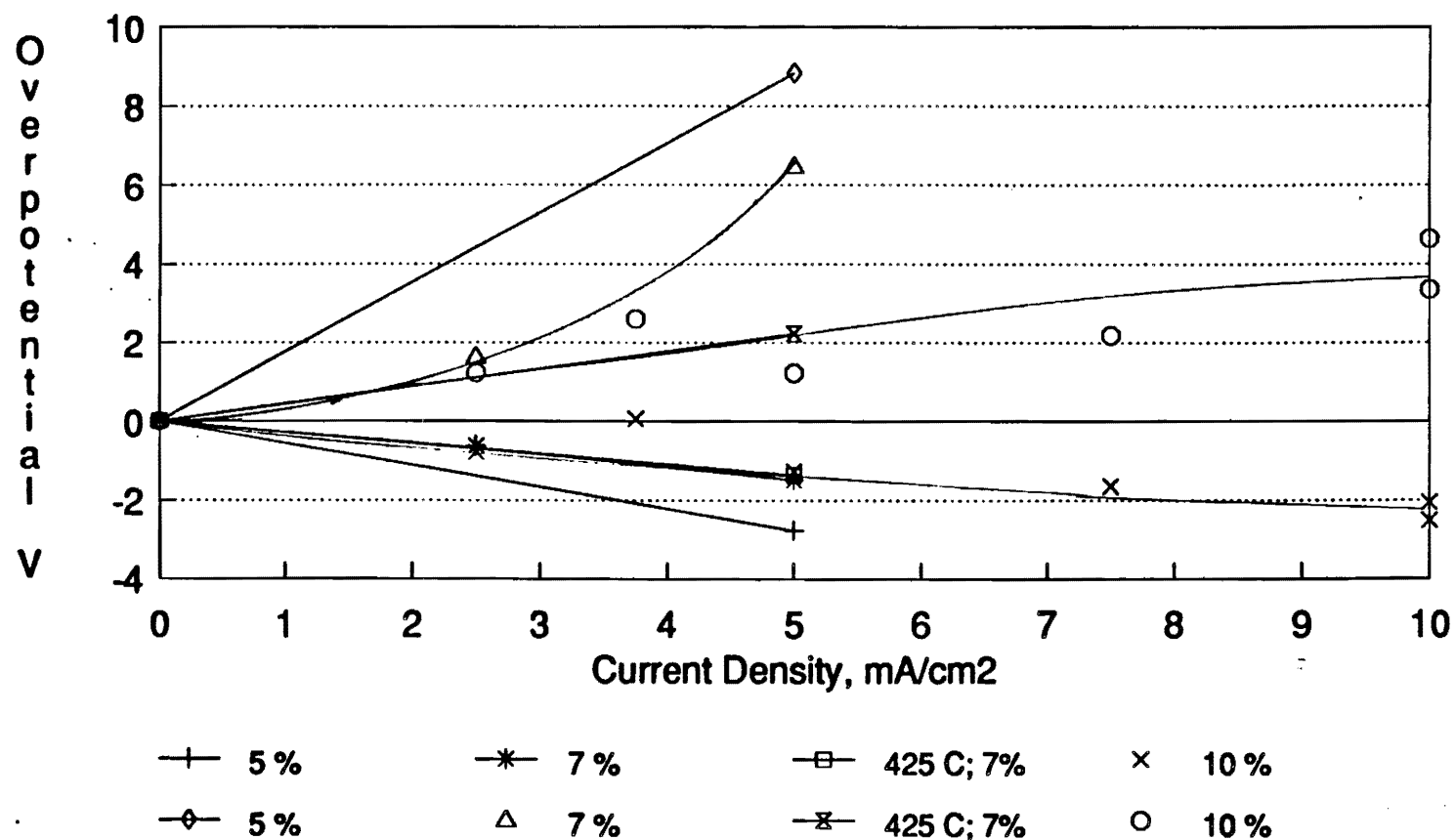


Figure 13. Polarization curves after 60 minutes of applied current.

to determine  $i_0$ , the exchange current density. The other parameters are  $R$ , the gas constant,  $n$ , the number of electrons involved in the charge transfer reaction, and  $F$ , Faraday's constant. Data from the present run was reduced using equation (2) and is presented in Table I, along with data

from Franke<sup>2</sup>, who used  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$

**Table I. Exchange current densities.**

electrodes. These data show that the electrochemical kinetics at the cathode have improved 50% under the same conditions of electrolyte composition and temperature (5%, 400° C), further substantiating the improved performance of the lithiated nickel oxide electrodes.

wt. % $\text{V}_2\text{O}_5$	T, ° C	$i_0$ , mA/cm <sup>2</sup>
5%	400	0.052
7%	400	0.115
7%	425	0.106
10%	400	0.133
5%, Franke <sup>2</sup>	400	0.033

With an increase in  $\text{V}_2\text{O}_5$ , the exchange current density has increased four times. While there is some improvement here, free electrolyte studies have shown the exchange current density to be 30 mA/cm<sup>2</sup> in  $\text{SO}_3$ -saturated electrolyte. The discrepancy here can be attributed to partial flooding of the electrode pores and diffusional resistances.

The next full cell tests used electrodes made by laminating an ERC and Fibrex electrode together. The individual pieces were cut and pressed together so that they would fit flush with the surface of the housings. The composite electrodes were then lithiated and oxidized in the housings at 575° C in pure  $\text{O}_2$ . The impetus for using these combination electrodes was to determine if increasing the surface area of the

electrode could stop the net generation of  $\text{SO}_2$  from the cathode side of the cell. Net generation of  $\text{SO}_2$  was not seen with the ERC material, but excessive flooding was.

During preparation, the upper electrode warped slightly, causing problems with the wet seal during this run. The electrolyte was an homogeneous mixture of 10 wt. %  $\text{V}_2\text{O}_5$  in  $\text{K}_2\text{S}_2\text{O}_7$  to further enhance the oxidation of electrochemically generated  $\text{SO}_2$ . Unfortunately, a poor gas seal and gas crossover prevented acquisition of removal data during the run. Upon post-mortem analysis, the membrane was found to have cracks throughout, a condition only seen in non-laminated tapes. However, this cracking may also be due to the high ceramic content (59 vol. %).

The same electrodes and electrolyte were used in the next full cell study. This time a laminated tape of 30 vol % and 59 vol % ceramic tapes was used. After burnout and electrolyte infiltration, good seals were formed between the membrane and both housings, but again, electrical contact between the lead and top electrode suffered, causing resistances 15 times higher than those found between the bottom electrode and its lead wire.

### Summary

The results of the successful experiment above show that the electrochemical process is capable of removing 90% of inlet  $\text{SO}_3$ , the product of the catalytic oxidation of  $\text{SO}_2$ . For all levels of  $\text{V}_2\text{O}_5$  tested,  $\text{SO}_3$  removal reached greater than 80%, with removals in excess of 90% for 10 wt.%  $\text{V}_2\text{O}_5$ .

The greatest improvement found in the present configuration is in the area of polarization performance. Franke<sup>3</sup> presented polarization data up to a maximum of

2 mA/cm<sup>2</sup> (40 mA), with a cathodic overpotential of 2.7 V. The present curves show much higher current densities (10 - 20x) for the same or lower overpotential. This improved polarization is due to a number of factors. First, the lithiated NiO electrodes remain stable during the run, compared to the perovskite used by Franke. Secondly, the present cathode has a much lower actual to superficial area ratio (~25) compared to the perovskite (~200). And, third, the pores are larger in the NiO. These last two factors may reduce the level of electrode pore flooding and leave more surface area exposed to gas than with the perovskite.

The present removal cell configuration also shows a much extended operating lifetime. Using tape cast membranes and lithiated nickel oxide electrodes, this run lasted 28 days and was voluntarily terminated, with only minor degradation in electrolyte resistance and polarization performance. Post-mortem analysis showed low levels of NiO corrosion products, which were explained in the last quarterly report. Runs with perovskite electrodes and hot-pressed membranes typically produced quality data for 4 days, with an increase in electrolyte resistance and polarization during the run.

A new problem was detected in the above data. The release of SO<sub>2</sub> at the cathode shows insufficient V<sub>2</sub>O<sub>5</sub> activity in the catholyte, allowing electrochemically-generated SO<sub>2</sub> to escape from the electrolyte and be carried away with the gas stream. Increasing the vanadia loading reduced this effect, but to an insufficient level to permit stoichiometric removal of inlet SO<sub>x</sub>. It should be noted that in several of the runs, SO<sub>3</sub> concentrations dropped to below the limits of detection, so that little SO<sub>3</sub>



would be released during power plant operation. The problem of  $\text{SO}_2$  release may be handled by well-mixing of the electrolyte preparation and will be addressed in future experiments. Another approach is to optimize the electrode structure such that the actual current density (not superficial) is reduced, which will in turn reduce the mass flux of  $\text{SO}_2$  out of the electrode. Other options include platinizing the electrode surface and conducting the removal in stages, with intermediate oxidation of  $\text{SO}_2$ . All of these solutions require further study.

### **Planned work for next quarter**

To overcome the  $\text{SO}_2$  generation seen above, the same two approaches will be used. To overcome the electrical contact problems, stainless steel 316 housings will be machined. This material, when oxidized, remains electrically conductive. The corrosion resistance and electrical conductivity of this material is still to be determined in a full cell test. The advantage of conductive housings is that electrical current will be conducted to the electrode by way of the baffles and support ridge, which possess more than  $1.5 \text{ cm}^2$  of contact area, compared to 20 cm of 0.25 mm platinum wire. If corrosion reduces electrical conductivity of the housings, they will be nickel plated, lithiated and oxidized in a manner similar to that of the electrodes.

## II. H<sub>2</sub>S Removal Cell

### Introduction

This electrochemical removal cell cleans a product gas of H<sub>2</sub>S by electronating the most easily reduced component of the stream. In coal synthesis gas, this is H<sub>2</sub>S:



A membrane which contains sulfide ions in a molten state will act to transport sulfide across to the anode. If the membrane is capable of preventing diffusion of hydrogen from the cathode side, an inert sweep gas such as N<sub>2</sub> can be used at the anode to carry away oxidized sulfide ions as vaporous S<sub>2</sub>:



### Research Summary

Work has continued in the polishing applications of the electrochemical membrane separator with successful removal of H<sub>2</sub>S from 100 ppm down to below analytical limits of the gas chromatograph (approximately 2 ppm). Development work has centered around demonstrating tape casting technology as an economical means for the manufacture of gas-impermeable ceramic matrixes for retaining the electrolyte between the two electrodes of the cell and examining behavior of Molten Carbonate Fuel Cell (MCFC) electrodes, namely lithiated nickel and lithiated nickel oxide, in the run environment.

It has been demonstrated that tape casting technology can be used as an industrial scale method for membrane manufacture. It has also been demonstrated that MCFC electrodes can be used successfully as electrode materials for polishing

applications of the cell (less than 100 ppm  $\text{H}_2\text{S}$  down to sub-ppm levels).

## **A. Experimental Run Results**

### **Run 41**

This was the first attempt at using an MCFC membrane as the separator between the process and sweep sides of the separator. A MCFC tile, obtained from IGT (Institute of Gas Technology) was used as the membrane. The tile had  $\text{LiAlO}_2$  as the matrix material with eutectic composition  $\text{Li}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  as the electrolyte. The cathode was carbon and the anode was lithiated NiO. Gas composition was 1.46%  $\text{CO}_2$ , 98 ppm  $\text{H}_2\text{S}$ , 3.6%  $\text{H}_2\text{O}$ , balance  $\text{CH}_4$ .

The run was terminated before any useful data was obtained due to a burn-out in the electrical leads supplying power to the furnace.

### **Run 42**

This second attempt at using MCFC tiles as membrane materials was more successful. Once again, the tile had  $\text{LiAlO}_2$  as the matrix material with eutectic composition  $\text{Li}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  as the electrolyte. The cathode was carbon and the anode was lithiated NiO. Carbon was used as the cathode material in an attempt to eliminate the sulfide capacitance effects as Ni is converted to NiS or  $\text{Ni}_3\text{S}_2$  (as described in Run 39, March 1 to June 30 report) The NiO anode was manufactured by soaking Ni electrode material from ERC in 1M LiOH and then heating to  $650^\circ\text{C}$  overnight. Weight analysis of the resulting electrode showed greater than 98%

conversion of Ni to NiO. The process gas for this run, a simulated natural gas, had a composition of 1.44% CO<sub>2</sub>, 97 ppm H<sub>2</sub>S, 4.4% H<sub>2</sub>O, and the balance CH<sub>4</sub>.

Completely selective removals of H<sub>2</sub>S as high as 98% (97 ppm down to less than 2 ppm) were observed with negligible cross-cell potential and 2.5 mA applied to the cell (0.32 mA/cm<sup>2</sup>) at a process flow rate of 200 cc/min. This corresponds to 98% current efficiency. At higher process flow rates 75.2% removal of H<sub>2</sub>S (97 ppm down to 24 ppm) with 5 mA applied to the cell (current density of .64 mA/cm<sup>2</sup>) and a process flow rate of 450 cc/min was observed. This current density should have given 88% removal. This corresponds to a current efficiency of 85%. Figure 1 shows the H<sub>2</sub>S removal vs applied current.

An analysis of the electrolyte from this run showed the sulfide level at 6.7% and the carbonate level at 93.3%. This corresponds to predicted values of 2.8% sulfide and 97.2% carbonate. This discrepancy between the predicted values and the actual values can be explained by the presence of an unknown slag found in the crucible after ashing to recover the BaSO<sub>4</sub>; the BaSO<sub>4</sub> precipitate was not adequately washed during the filtering process. X-ray analysis of the membrane material shows only LiAlO<sub>2</sub> and the hydrated forms LiOH\*2Al(OH)<sub>3</sub>\*xH<sub>2</sub>O and Li<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>\*xH<sub>2</sub>O present. Evidently, the low sulfide levels were not sufficient to cause attack of the LiAlO<sub>2</sub> matrix. The hydrated species of LiAlO<sub>2</sub> were no doubt formed when the membrane material was washed overnight in water to dissolve the electrolyte species out of the matrix. X-ray analysis results are presented graphically in Figure 2.

### Run 43

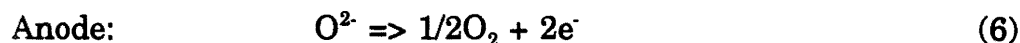
This experimental run was the first successful run which used a completely tape cast membrane MgO matrix. The electrolyte was eutectic potassium/lithium carbonate which was added after the binder material was burned out. Both the cathode and the anode in this experiment started out as lithiated NiO. The process gas for this experiment started out as 1.4% CO<sub>2</sub>, 3.9% H<sub>2</sub>O, balance methane. Later in the run, 1.38% CO<sub>2</sub>, 92 ppm H<sub>2</sub>S, 3.9% H<sub>2</sub>O, balance methane was used.

The ceramic membrane was manufactured by mixing 16.5 grams MgO, 83.3 grams Metoramics K565-4 Acrylic Binder System (24.9 wt% acrylic polymer), 1 gm Metoramics M-1111 releasing agent, and 1 gm Metoramics M-1114 surfactant. The exact composition of these tape casting agents are proprietary to Metoramics. These were mixed in a ball mill overnight and poured out onto M-1111 coated glass. Air drafts across the surface of the cast were prevented by placing a cardboard sheet over the cast with a 4mm thick spacing between the surface of the cast and the cardboard sheet. This allowed uniform evaporation of the solvents from the cast since the convective effects of room air were minimized. The resulting tape was 42.1 wt% MgO with the remainder acrylic binders. When the binders were burned away, this corresponded to 88.1 vol% free volume.

Three inch diameter, 0.5mm thick membranes were cut from the tape and three of these were layered in the cell. Pure O<sub>2</sub> was blown across the cathode and anode sides of the cell and the assembly was heated to 375°C overnight. The next day, after smoking from the burning binder material was no longer observed, fuel gas (1.40 % CO<sub>2</sub>, 3.9% H<sub>2</sub>O, balance CH<sub>4</sub>) was started to the cathode side of the cell and

N<sub>2</sub> was started to the anode. Electrolyte was added, 20.8 grams, through the reference electrode hole in the top of the cell assembly. Only 17.3 grams were required based on the free volume of the membrane, but more was added to compensate for electrode wetting, wet seal formation with the MACOR housings, and spillage during the adding process.

Upon adding electrolyte to the cell, cross-cell resistance dropped from infinite to 0.35 ohms. Initial tests of the cell performance were centered around CO<sub>2</sub> transport. With applied currents of 400 mA (50.5 mA/cm<sup>2</sup>) CO<sub>2</sub> levels dropped from 1.4% to 0.6% (57.1% removal). CO<sub>2</sub> removal data is presented in Figure 3. This corresponds to a current efficiency of only 52%. Since the cross-cell potential was stable at only -1.36 volts, an alternative current path was probably present. Since the CO<sub>2</sub> present in the anode corresponds to the CO<sub>2</sub> removed from the anode to within 75%, there must be transport present by a species that we are not presently analyzing for. This may possibly be explained by the following mechanism:



These two half cell reactions sum to the same overall cell reaction as that for carbonate transport:



The only question is that the O<sup>2-</sup> ion is highly basic and should react with CO<sub>2</sub> to form

$\text{CO}_3^{2-}$ . If this were the case,  $\text{CO}_2$  would be removed in amounts closer to stoichiometric. This has not been observed. Possible explanations for this lack of  $\text{CO}_2$  transport is that the reduction of  $\text{NiO}$  to  $\text{Ni}$  in equation (4) takes place below the electrode/electrolyte interface and thus the  $\text{O}^{2-}$  ion is not exposed to sufficient  $\text{CO}_2$  to form appreciable quantities of  $\text{CO}_3^{2-}$ . Thermodynamic analysis shows that reaction (4) takes place at a standard potential of only -1.596 volts with respect to the  $\text{O}_2/\text{CO}_2$  reference electrode. Reaction (6) takes place at a standard potential of only 0.773 Volts with respect to the reference electrode (around the same potential as the oxidation of sulfide). Thus the electrochemical potentials for the above mechanism are on the proper order of magnitude.

$\text{H}_2\text{S}$  was then fed into the system gas by bleeding in a contaminated gas stream to obtain a final gas composition of 1.38%  $\text{CO}_2$ , 92 ppm  $\text{H}_2\text{S}$ , 3.9%  $\text{H}_2\text{O}$ , and the balance  $\text{CH}_4$ . Removal was demonstrated to a level of less than 2 ppm with an applied current of 5 mA (current density of  $0.63 \text{ mA/cm}^2$ ) and a process stream flowrate of 415 cc/min.  $\text{H}_2\text{S}$  removal data is presented in Figure 4. This corresponds to 100% current efficiency. It should be noted that nearly 5 days exposure to the  $\text{H}_2\text{S}$  contaminated stream was required to sufficiently sulfide the electrolyte so that any effect with current at all could be seen; current was applied for 24 hours before a sufficient sulfide gradient within the membrane was established to bring cathode process gas concentrations below 2 ppm. At these gas phase concentration levels, the equilibrium sulfide concentration of the membrane is very slow to be reached as the molar flowrate of sulfide in the gas phase is very small. Cross-cell potentials hovered

around -0.650 Volts.

The cell was shut down after 222 hours of operation when gas supplies ran out. X-ray analysis of the electrode materials showed that the cathode was a mixture of Ni, NiO, Ni<sub>3</sub>S<sub>2</sub>, and NiS. Cathode X-ray data is presented in Figure 5. The presence of both Ni and NiO in the cathode suggests possible support for the above current transport mechanism through the O<sup>2-</sup> ion at higher cross-cell potentials. The anode was almost entirely NiO with some traces of Ni present. X-ray data for the anode is presented in Figure 6. Post-run examination of the anode exit gas-flow tube showed a brownish-yellow coating of the interior wall of the tube at a position just outside of the cell furnace. This is the location that condensing sulfur would be expected to collect. The coloration and location of this tube discoloration suggests that it is amorphous sulfur. Chemical analysis on this substance is currently in progress.

## Summary

The polishing applications of the removal cell have been confirmed with H<sub>2</sub>S levels dropping below 2 ppm (See Figures 1 and 4) in simulated natural gas streams. Current efficiencies are close to 100% for H<sub>2</sub>S removal but they seem to fall off with increasing current for CO<sub>2</sub> removal. This is possibly explained by an O<sup>2-</sup> transport mechanism which could take place at electrochemical potentials comparable to that for CO<sub>3</sub><sup>2-</sup> transport. The presence of both NiO and reduced Ni suggests a possible catalytic role for the cathode material with H<sub>2</sub>O as the source of oxygen in the gas phase.



Tape casting of membrane materials has been successfully demonstrated and the longest period of continuous operation of the  $\text{H}_2\text{S}$  removal cell has been increased to 222 hours.

### **Planned Work for Next Quarter**

Stainless steel cell housings will be manufactured and experimentation will begin with simulated coal gasification process streams. More work will be done with Metoramic binder systems in refining the tape casting process for membrane manufacture. The thermodynamics of the Ni electrodes will be further examined. Work will also continue on the polishing applications of the cell, with gases contaminated with only 10 ppm  $\text{H}_2\text{S}$  which will be polished to less than 2 ppm.

Work will also begin on mathematical modeling of the removal cell system.

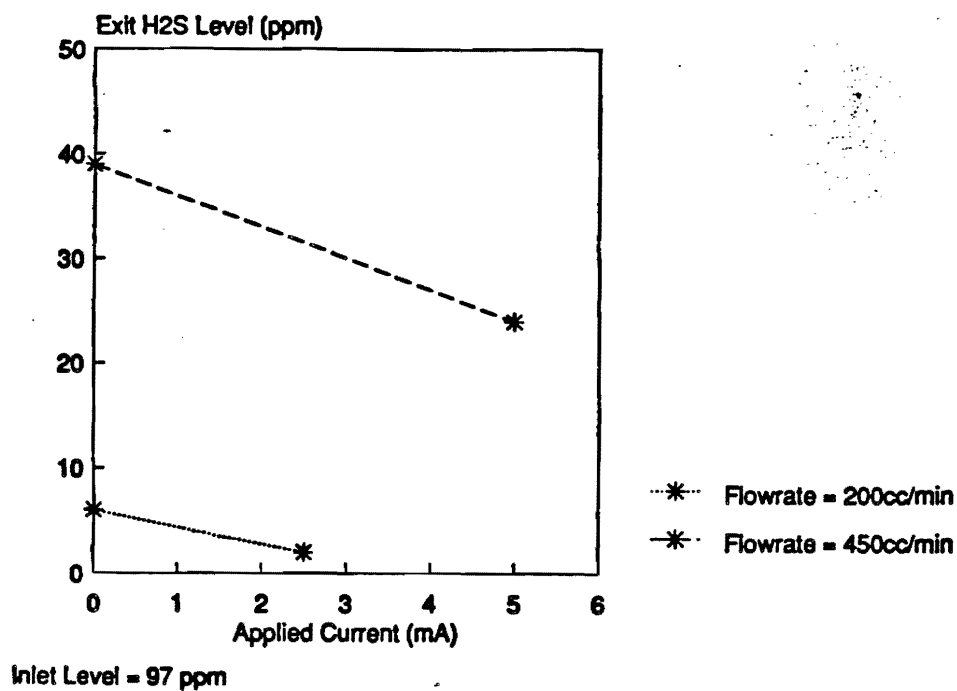


Figure 1.  
H<sub>2</sub>S Level vs Applied Current, Run 42.

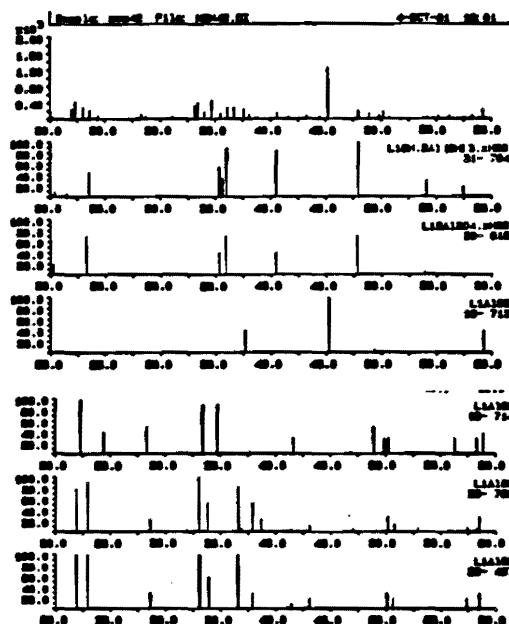


Figure 2.  
X-Ray Diffraction Pattern, Membrane Matrix, Run 42.

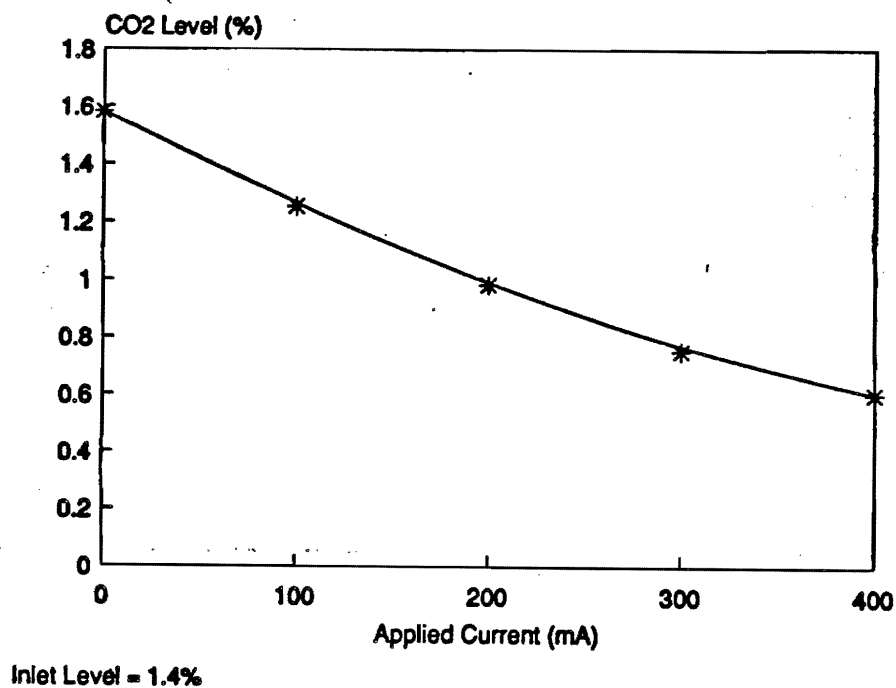


Figure 3.  
CO<sub>2</sub> Level vs Applied Current, Run 43.

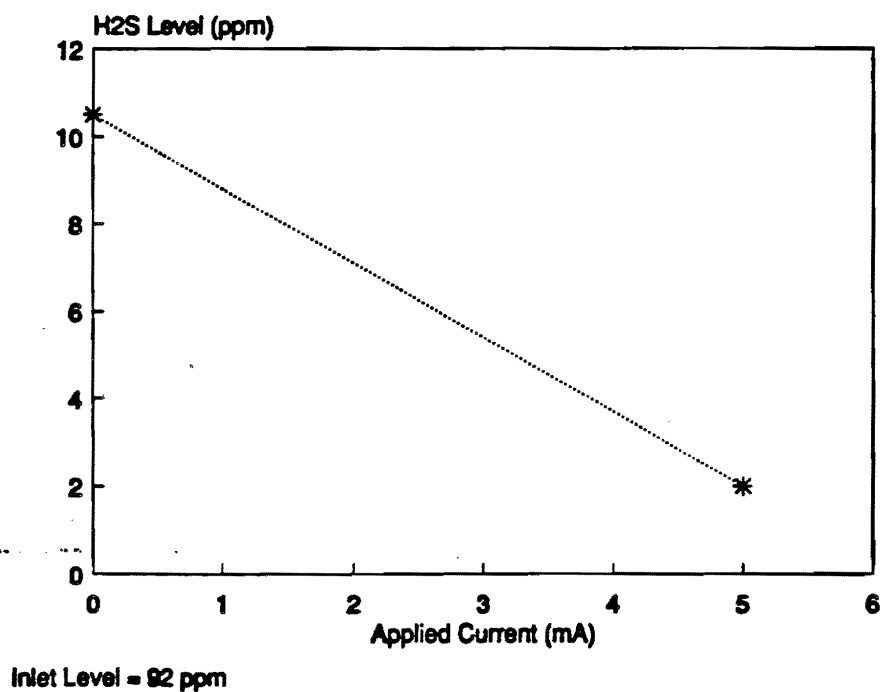


Figure 4.  
H<sub>2</sub>S Level vs Applied Current, Run 43.

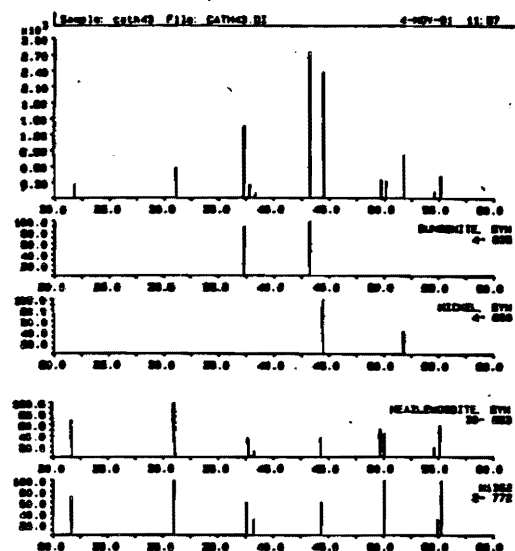


Figure 5.  
X-Ray Diffraction Pattern, Cathode, Run 43.

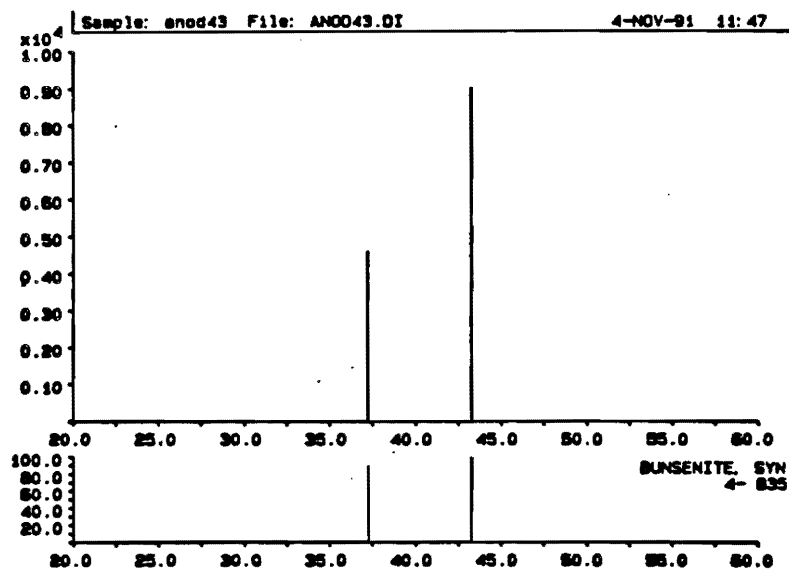


Figure 6.  
X-Ray Diffraction Pattern, Anode, Run 43.

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Quarterly Progress Report:  
High Temperature Membranes for  
H<sub>2</sub>S and SO<sub>2</sub> Separations  
Grant DE-FG22-90PC90293  
October 1, 1991 - December 31, 1991

by

Professor Jack Winnick  
Georgia Institute of Technology  
School of Chemical Engineering  
Atlanta, Georgia 30332-0100

## **Purpose and Goals of Research**

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  cell and the  $\text{SO}_2$  cell require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.



## **I. H<sub>2</sub>S Removal Cell**

### **Introduction**

This electrochemical removal cell cleans a product gas of H<sub>2</sub>S by electronating the most easily reduced component of the stream. In coal synthesis gas or natural gas, this is H<sub>2</sub>S:



A membrane which contains sulfide ions in a molten state will act to transport sulfide across to the anode. If the membrane is capable of preventing diffusion of hydrogen from the cathode side, an inert sweep gas such as N<sub>2</sub> can be used at the anode to carry away oxidized sulfide ions as vaporous S<sub>2</sub>:



### **Research Summary**

We have demonstrated that tape casting technology can be used as an industrial method for membrane manufacture. Work has recently concentrated on the application of this process to polishing H<sub>2</sub>S from 100 ppm down to below the analytical limits of the gas chromatograph (approximately 2 ppm) for use with Coal Gasification technology. Use of Molten Carbonate Fuel Cell (MCFC) materials has been examined, and use of more industrial suited cell housing materials, namely 316 stainless steel, has been examined.

## A. Experimental Run Results

### Run 44

This was our first attempt at the application of this technology to coal synthesis gas  $H_2S$  polishing. The tapes were manufactured using established tape casting methods. 16.5 grams of  $MgO$ , 83.3 grams of Metoramics binder system K565-4, 1 gram of Metoramics releasing agent M-1111, and 1 gram of Metoramics surfactant M-1114 were ball milled for 24 hours and then poured out on M-1111 coated glass. After the solvent had volatilized out, eight 3 inch diameter membranes were cut from the tape, each with a thickness of approximately 0.03 cm.

The actual membrane used in this experimental run was a combination of three of these membranes layered together with the acrylic binder burned out under an  $O_2$  atmosphere. Eutectic composition Li/K carbonate (62% Li, 38% K) was then wicked into the membrane in-situ. Both the anode and cathode were lithiated  $NiO$ .

The composition of the gas fed to the cell was 13.2%  $CO_2$ , 33.2%  $H_2$ , 48.8%  $CO$ , 4.8%  $H_2O$ , and 100 ppm  $H_2S$  (assuming that the gas has gone to its equilibrium composition). This corresponded to an electrolyte equilibrium composition of 99.6% carbonate and 0.4% sulfide at an operating temperature of 650°C. Since sulfide is the current-carrying species, this low equilibrium sulfide level brought up the question of whether the process limiting current density would still be determined by gas phase mass transport of  $H_2S$  to the electrode/electrolyte interface (as in all previous experiments) or if it would now be determined by transport of sulfide ions through

the molten electrolyte. A theoretical comparison of the transport in the molten electrolyte to transport in the gas phase was performed in the following manner:

Current carried through the electrolyte by sulfide ions is described by,

$$i_d = 2FD\rho\Delta C/\Delta x \quad (7)$$

where  $\rho$  is the molar density of the electrolyte in the ceramic membrane (0.0208 gmole/cc),  $\Delta C$  is the sulfide concentration gradient through the electrolyte (0.0044) assuming equilibrium sulfide concentration at the cathode and essentially zero concentration at the anode.  $\Delta x$  is the membrane thickness (0.1 cm),  $D$  is the sulfide diffusivity (approximated at  $10^{-5}$  cm<sup>2</sup>/sec), and  $F$  is Faraday's constant 96500 coulombs/equivalent. These conditions give a membrane limiting current density of 1.8 mA/cm<sup>2</sup>.

Current carried by mass transport of H<sub>2</sub>S to the electrode surface through the gas phase is calculated using the following equation:

$$i_d = 2Fk\rho(y_{in}-y_{out})/\ln(y_{in}/y_{out}) \quad (8)$$

where  $k$  is the mass transfer coefficient and is approximated based on channel geometry and gas temperature, density, and viscosity ( $k = 12.9$  cm/sec),  $\rho$  is the molar density of the gas phase ( $1.32 \times 10^{-5}$  gmole/cm<sup>3</sup>),  $y_{in} = 9.91 \times 10^{-5}$ , and  $y_{out} = 1 \times 10^{-5}$ . These conditions give a gas phase limiting current of 1.3 mA/cm<sup>2</sup>. Thus, sulfide transport limitations in the gas phase are seen to be comparable to those in the electrolyte.

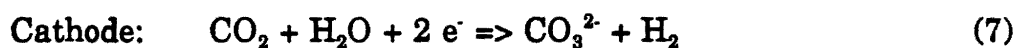
The run itself was terminated before any removal data was collected. Several factors contributed to the decision to terminate the experiment. First of all, the

control relay on the furnace froze shut, causing the temperature to overshoot the acrylic burnout temperature of 350°C by over 300°. This damaged the membrane before the electrolyte was added and allowed process gas to cross over and mix with the sweep gas. The gas chromatograph results also became highly variable. It was found that a piece of the injection port septum broken off and fallen into the injection chamber, interfering with carrier gas flow. The GC was repaired and the run terminated due to gas cross-over through the damaged membrane.

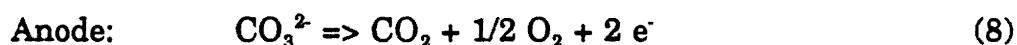
The cell was shut down after 14.8 hrs of operation.

#### Run 48

A properly operating cell will transport carbonate in the absence of H<sub>2</sub>S. It was decided to test for CO<sub>2</sub> transport in this experiment. Transport of CO<sub>2</sub> across the cell takes place by the following reactions:

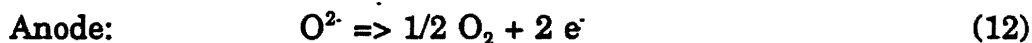
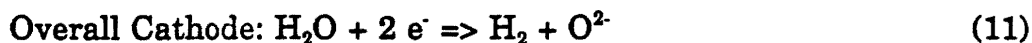


at the cathode and:



at the anode. Thus, CO<sub>2</sub> removed at the cathode and produced at the anode should stoichiometrically match the applied current. An alternative current carrying mechanism was proposed in our July 1, 1991 to Sept. 30, 1991 report. That mechanism is outlined below:





If this mechanism was taking place parallel to carbonate transport then  $\text{CO}_2$  would not be removed stoichiometrically with two Faradays of current.

This experimental run was the fourth run using coal gas and used two tapes of  $\text{MgO}$ , manufactured in a manner identical to that used in Run 44, and one mat of zirconia cloth as the membrane matrix material. The electrodes were both lithiated  $\text{NiO}$ . The acrylic binders were burned out under an  $\text{O}_2$  atmosphere and the  $\text{Li/K}$  eutectic composition electrolyte was added with the cell at run temperature.

$\text{CO}_2/\text{H}_2\text{O}$  species removal from the process gas as a function of applied current is shown in Figure 1. Examination of this figure shows that the removal of species is stoichiometric across the range of applied currents examined. Figure 2 shows the exit anode gas  $\text{CO}_2$  level as a function of applied current. Examination of this figure shows that  $\text{CO}_2$  removed from the cathode process gas was transported across the cell and produced at the anode. The calculated  $\text{CO}_2$  levels, based on current carried by the oxidation of the  $\text{CO}_3^{2-}$  ion, tracks the observed  $\text{CO}_2$  values very closely. Figure 3 shows the overpotential of the cell with applied current. Examination of this data shows that the cross-cell potential crosses the -1 volt cathode to anode threshold potential required for carbonate transport at lower currents than previously seen with high levels of  $\text{H}_2\text{S}$  present (>1000 ppm). We see that in the higher  $\text{CO}_2$  concentrations found in coal gasification synthesis gas,  $\text{CO}_2$  removal is stoichiometric with applied current.

When these results are compared to the CO<sub>2</sub> removal study done in Run 42 (July 1, 1991 to Sept. 30, 1991 report), we see that at lower CO<sub>2</sub> levels (1.4% CO<sub>2</sub> in natural gas as compared to 13% CO<sub>2</sub> in coal gas) the possibility of O<sup>2-</sup> transport may exist. The higher CO<sub>2</sub> content in coal gas provides enough CO<sub>2</sub> to the electrolyte/electrode interface that the highly basic O<sup>2-</sup> ion is attacked by CO<sub>2</sub> to form CO<sub>3</sub><sup>2-</sup>. Thus, even if NiO is acting as a catalytic species for production of the O<sup>2-</sup> ion as suggested by the results from run 42, in this application the higher CO<sub>2</sub> levels cause the formation of CO<sub>3</sub><sup>2-</sup> and CO<sub>2</sub> is still transported stoichiometrically with applied current.

Instead of adding eutectic Li/K carbonate as a powder and allowing it to melt down the reference electrode hole as in previous runs, electrolyte was melted external to the cell and poured directly down the reference electrode hole in this experiment. Cell seals were initially excellent on both sides of the cell, but flow out the anode side of the cell eventually stopped. Shortly after the anode flow stopped, cell cross-flow was observed and the cell run was terminated. A post mortem examination of the cell showed that electrolyte had run out of the membrane and into the anode side flow channel and down the tube. Once gas flow had forced a bubble of electrolyte outside the furnace it froze and blocked the tube, clogging the flow. The run was then terminated after 6.75 hours.

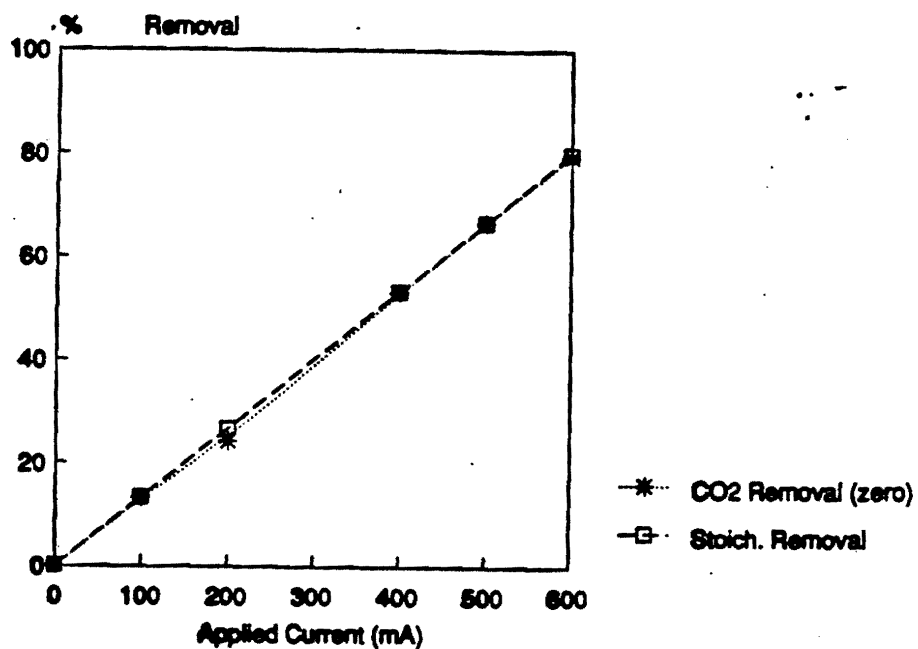


Figure 1.  
 $\text{CO}_2/\text{H}_2\text{O}$  Species Removal vs Current.

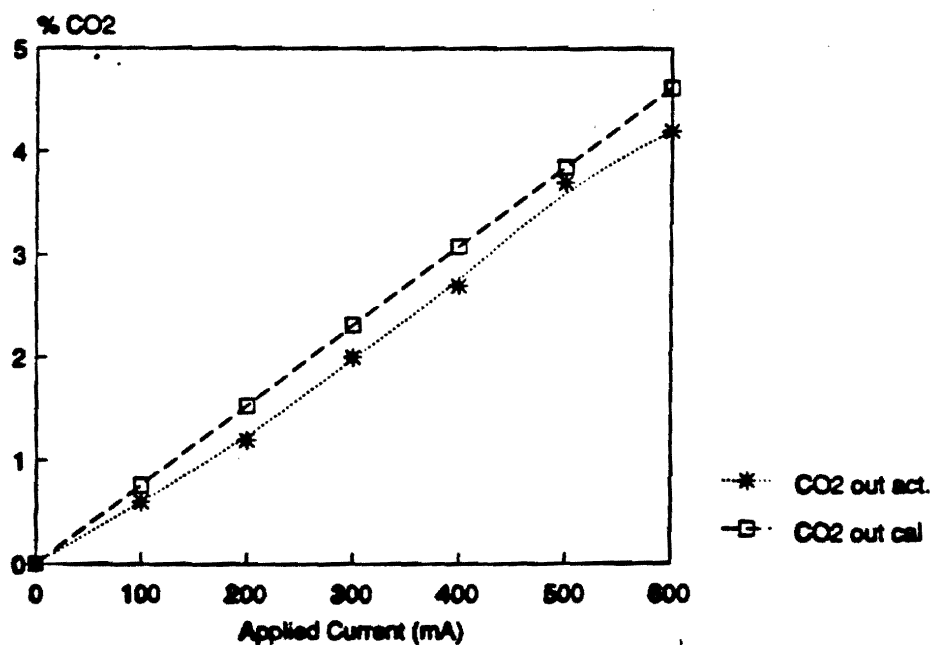


Figure 2.  
Anode  $\text{CO}_2$  Production vs Applied Current.

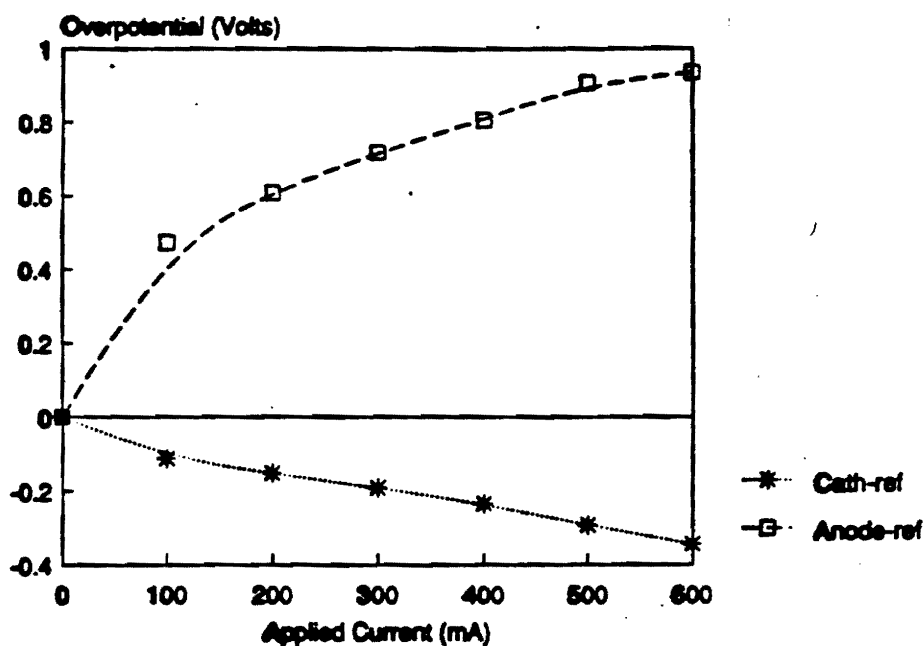


Figure 3.  
Cell Overpotential vs Applied Current.

### Summary

Marginal success with the application of tape casting technology for the manufacture of membranes for the polishing of  $\text{H}_2\text{S}$  from simulated coal gasification process streams has been shown. No evidence was found to show the presence of the  $\text{O}^{2-}$  transport mechanism proposed in the previous report at these  $\text{CO}_2$  concentration levels.



**Planned Work for Next Quarter**

Work will continue on the application of tape cast membranes to the polishing of coal gasification process streams. Attempts at achieving equilibrium sulfide levels in the electrolyte will be made in an effort to show the full electrochemical removal effects of this technology. Steady state operation of a tape cast cell membrane within a stainless steel housing will be the main goal.

## II. SO<sub>x</sub> Removal Cell

### Introduction

The key to successful application of this technique is the development of a membrane capable of supporting a current density of 50 mA/cm<sup>2</sup> at total voltages near 1 Volt. Flooding of electrode pores by electrolyte has been identified as a problem, leading to increased polarizations over time. To reduce flooding, new materials and fabrication methods will be investigated to produce an homogeneous, theoretically dense membrane. The matrix material must have the proper particle size distribution to develop sufficient capillary forces to prevent the electrodes from withdrawing the electrolyte.

Three techniques will be used for construction of the membranes or 'tiles'. The first is 'hot-pressing' in which powders of matrix material and electrolyte are intimately mixed in a dry atmosphere. The second technique will involve manufacturing a sintered ceramic matrix without electrolyte present and then 'wicking' the molten electrolyte into the matrix voids by capillary action. In the third method, tape-casting, the matrix material, dispersed along with an organic binder in a liquid, is continuously formed into a dried tape on a substrate, maintained at constant thickness by an overhead doctor blade. The flexible, 'green' tape is cut to the desired size, the binder is burned out, and the matrix is sintered, leaving a rigid body of the porosity needed for the final tile. Electrolyte is then infiltrated at operating temperature.

## Research Summary

Work during the quarter concentrated on full cell testing to determine  $\text{SO}_2$  and  $\text{SO}_3$  removal capability and polarization performance. An effort was made to determine the possibility of using stainless steel housings and flow tubes as removal cell components. A minor emphasis was placed on electrode pore characterization by way of mercury porosimetry.

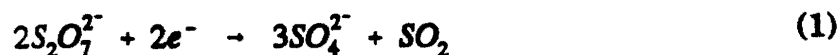
To evaluate stainless steel for the housings, a galvanostatic test was performed between two electrodes of SS 316, one pre-oxidized at  $525^\circ\text{C}$ , in a crucible of molten 5 wt.%  $\text{V}_2\text{O}_5$  in  $\text{K}_2\text{S}_2\text{O}_7$  to ascertain if SS 316 housings would survive the aggressive environment of electrolyte. Both pieces had about  $2\text{ cm}^2$  exposed to the electrolyte and handled up to 1000 mA with 12 V between them. At this extremely high current density, no pitting or electrical conductivity decrease was observed, but crystals of a sulfide did precipitate on the cathode. It is possible to reduce pyrosulfate to sulfide, but only under extreme voltage/current conditions such that oxygen or sulfur trioxide cannot get to the electrode surface. This phenomenon has never been seen in full cell studies with gas flowing past the electrodes. These new housings provide increased electrical contact with the electrodes along the 1/8" wide baffles, compared to the 0.010" (0.25 mm) Pt wire coil.

A full cell test performed during October, 1991, used a 49 volume percent silicon nitride tape cast matrix with 10 wt.%  $\text{V}_2\text{O}_5$  in  $\text{K}_2\text{S}_2\text{O}_7$  electrolyte, lithiated NiO electrodes and Macor housings with platinum leads. Some difficulty was encountered during start-up with insufficient electrolyte loading, but was corrected with

electrolyte additions through the reference electrode port in the top housing. Also, an excessive pressure drop was detected through the pre-oxidation catalyst bed at high flow rates.

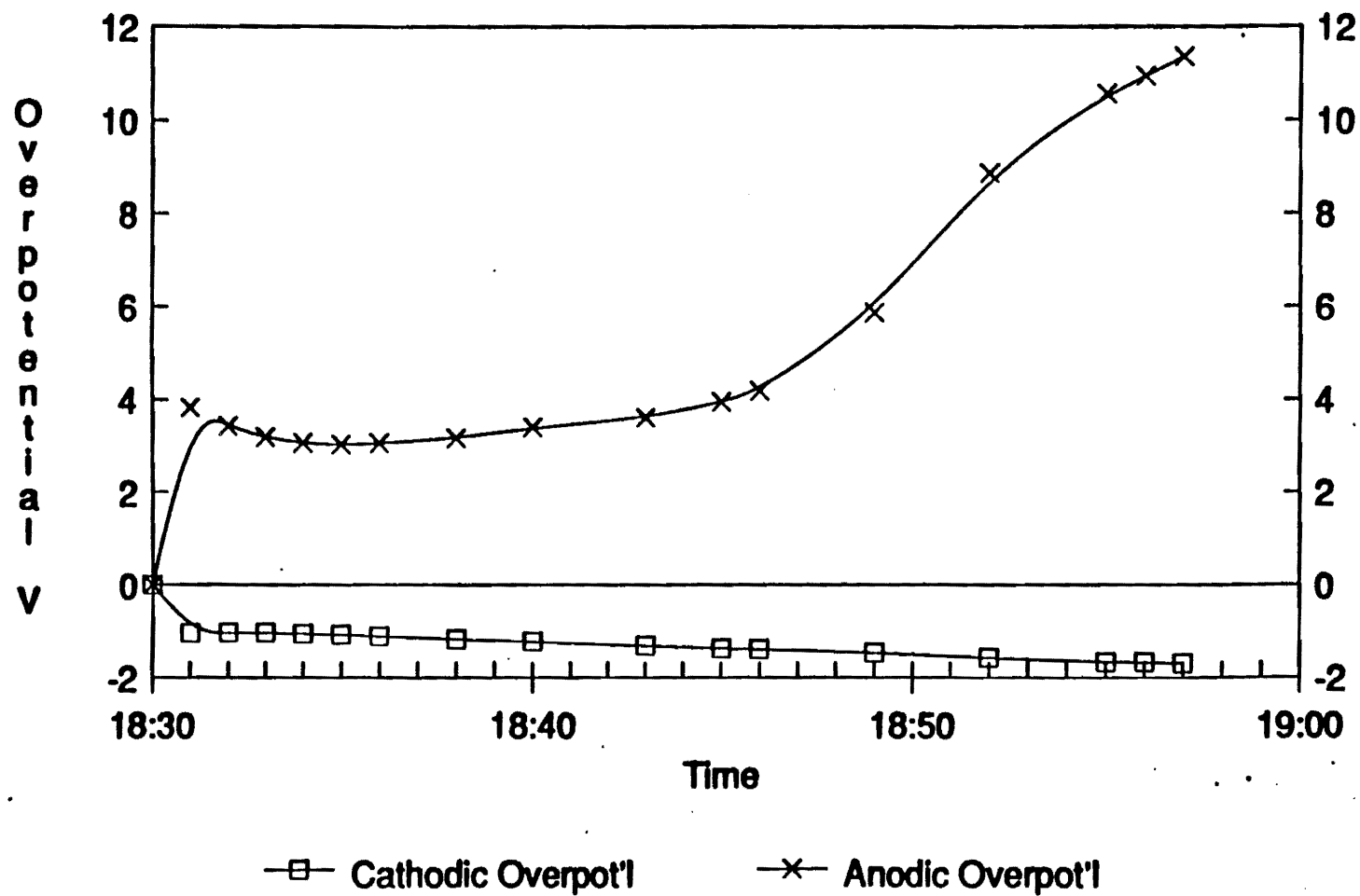
Figure 4 shows that the cathode performs well at 100 mA applied current (5 mA/cm<sup>2</sup>), but the anode shows an extreme performance decline over time. At the same time that the anodic overpotential increased, so did the anode to reference electrolyte resistance. This increase in resistance may be due to a loss of contact area between the electrode and lead wire, but was fully reversible at open circuit. Figure 5 shows that when electrolyte is added while current is applied, the overpotential at the anode drops significantly, confirming the loss of contact area as the cause of performance decline. The loss is due to either consumption of electrolyte or the formation of a frozen sulfate film between the electrode and lead or electrode and membrane. In either case, the current density is highest at this contact point, since the platinum leads are 0.25 mm in diameter. Later runs with the same cell configuration showed a much lower rate and magnitude of anodic polarization increase, most likely due to proper electrolyte content.

However, operation with 50 or 100 mA did produce some SO<sub>2</sub> at the cathode outlet, a possibility from the electrochemical reduction of pyrosulfate:



Generation of SO<sub>2</sub> was 11% at 50 mA and varied from 17% to 24% at 100 mA, relative to inlet flow rate. For SO<sub>3</sub>, removal (relative to equilibrium conversion of inlet

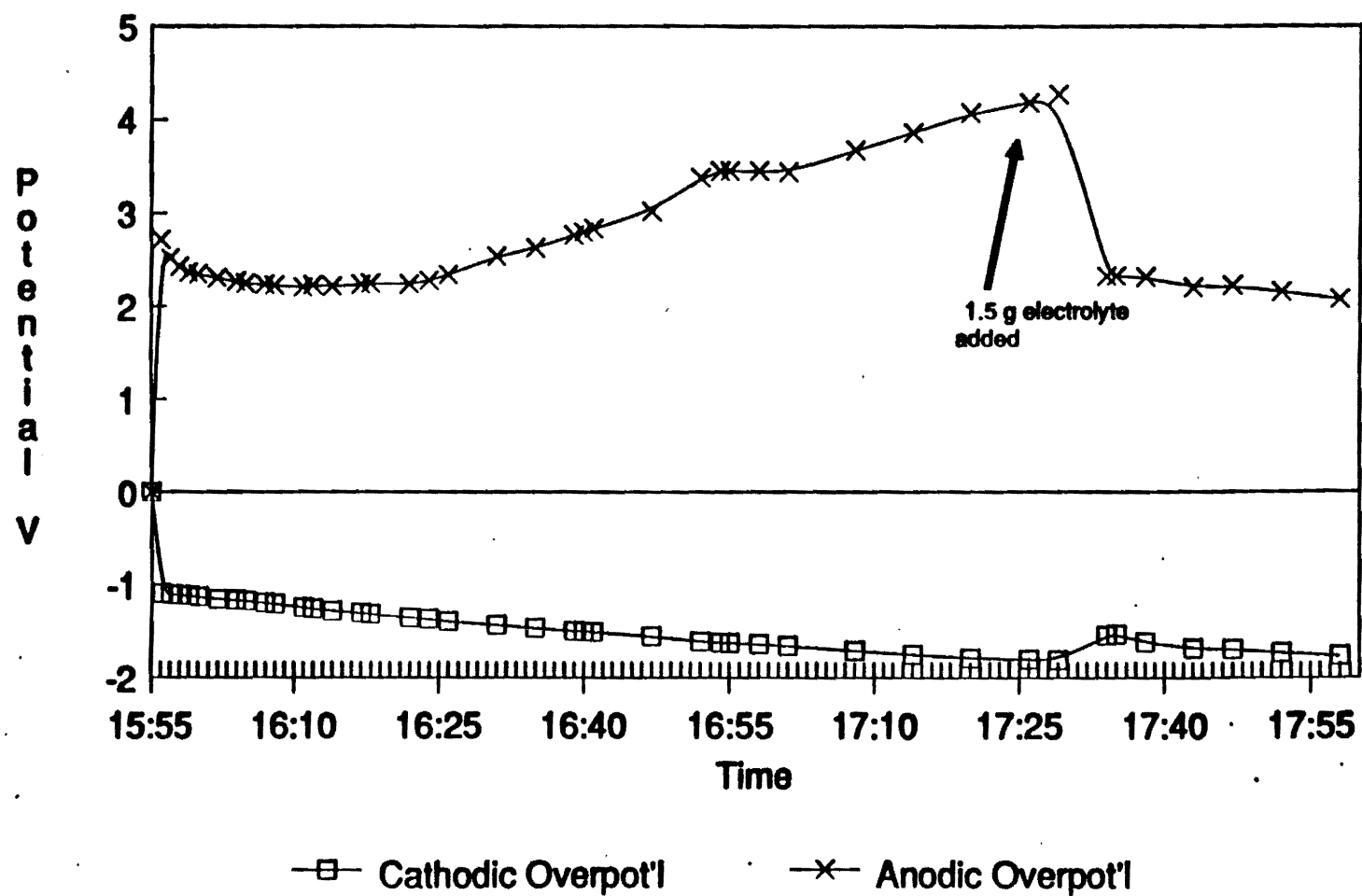
# Overpotentials



100 mA: no SO<sub>2</sub> detected

**Figure 4.** Polarization performance of NiO electrodes with 49 v/o ceramic membrane, 400° C.

# Overpotentials



100791; 100 mA

**Figure 5.** Polarization of electrodes, showing effect of electrolyte addition during applied current.

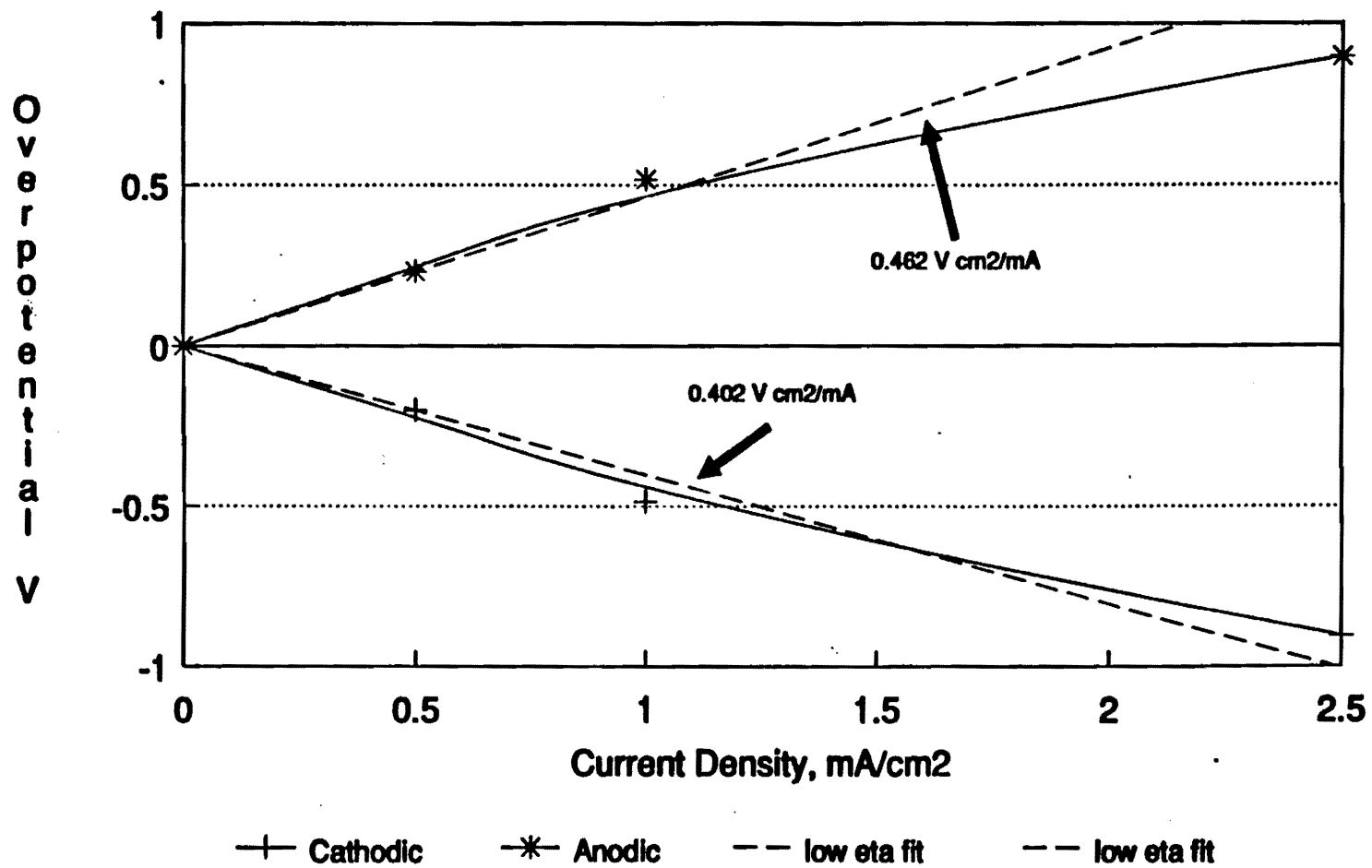
SO<sub>2</sub>) at 50 mA was 89% and 80% to 83% at 100 mA for a flow rate equal to 90% stoichiometric removal. One of the electrodes was kept in a vacuum desiccator and later analyzed with Electron Surface Characterization Analysis (ESCA). Investigation of the resulting peaks showed no Ni-S bonds present, negating the possibility of nickel sulfides or sulfates as corrosion products.

Once the new SS 316 housings had been machined, they were subjected to full cell evaluation. Inlet plumbing connections were made with Swagelok fittings and 1/4" SS 304 tubing. This run and the next one used a plug of platinized silica gel for the SO<sub>2</sub> pre-oxidation catalyst and suffered from excessive pressure drop at high flow rates. The outlet tubing consisted of a special flexible stainless bellows tube fused to a glass outlet line. This special fitting was required lest the effluent SO<sub>3</sub> would condense outside of the oven and possibly corrode the tubing, causing failure of the mass balance. Resistance measurements between the inlet tube and electrode were of the order of 3 ohms at room temperature, showing an exceptional conductivity.

A tape cast membrane was placed between the electrodes and slowly heated to 400° C in oxygen to burn out the polymer. Unfortunately, the membrane cracked, leading to excessive crossover of gases. Several other attempts identified that the polymer was softening during heat-up and sticking to the housings. This difficulty was fixed by pre-heating the tape on a glass plate to 200° C to remove residual solvent and a portion of the polymer.

IR-corrected voltage - current characteristics at low currents were obtained and are shown in Figure 6. A linear extrapolation of the slope for the lower overpotential

# Polarization Performance



**Figure 6.** Polarization behavior of lithiated NiO after 15 mins. applied current.



portion of the curve showed that the exchange current density,  $i_0$ , at 400° C,

$$i_0 = \frac{RT}{nF} \left( \frac{di}{d\eta} \right) = 0.029V \left( \frac{di}{d\eta} \right) \quad (2)$$

was 0.072 mA/cm<sup>2</sup> at the cathode and 0.063 mA/cm<sup>2</sup> at the anode. These figures compare favorably with the exchange current densities of Franke<sup>1</sup>, who found a value of 0.030 mA/cm<sup>2</sup> in his full cell studies with perovskite electrodes and MgO-based membranes. Free electrolyte studies by Scott<sup>2</sup> determined an  $i_0$  value of 30 mA/cm<sup>2</sup>. Although there is some modest improvement with the present configuration, work is still required to boost the exchange current density to an adequate level.

The last full cell test of the quarter used a modified cell housing. A 1/4" diam. hole was drilled through the top housing into the gas flow channel. The modification was made so that molten electrolyte would be added onto the top electrode and distribute itself across the electrode and then into the membrane. The previous full cell experiment showed that when electrolyte was added through the reference port, some of the electrolyte flowed out from between the housings, resulting in lower electrolyte loadings.

The runs recounted above had high pressure drops through the pre-oxidation catalyst beds, so to fix this problem, the 1/4" tubing was cut and fitted to a 3/8" tube which contained the catalyst. This increase in diameter resulted in a 2.9x increase in cross-sectional area and a substantially decreased pressure drop at all flow rates investigated. However, some SO<sub>2</sub> bypassed the catalyst at the higher flows. A test of

bypass versus flow rate for the 1.745 g of 2% platinum-on-silica-gel used is shown in Figure 7. The curve shows a definite mass transfer limitation of  $\text{SO}_2$  to the catalyst surface. The asymptotic rate of reaction approaches  $95 \times 10^{-6}$  moles/min for this loading or  $54 \times 10^{-6}$  moles/min/g catalyst. Further experiments will use a higher mass of catalyst to increase conversion at higher flow rates.

A graph of instantaneous ohmic resistance in the electrolyte versus applied current for this cell, Figure 8, showed a dependence of ohmic loss with current. This can be attributed to capacitive effects at both electrodes. The "capacitors" in the electrolyte discharge, creating larger voltage drops. These measured voltage drops are then divided by the value of the previously applied current to give the resistance.

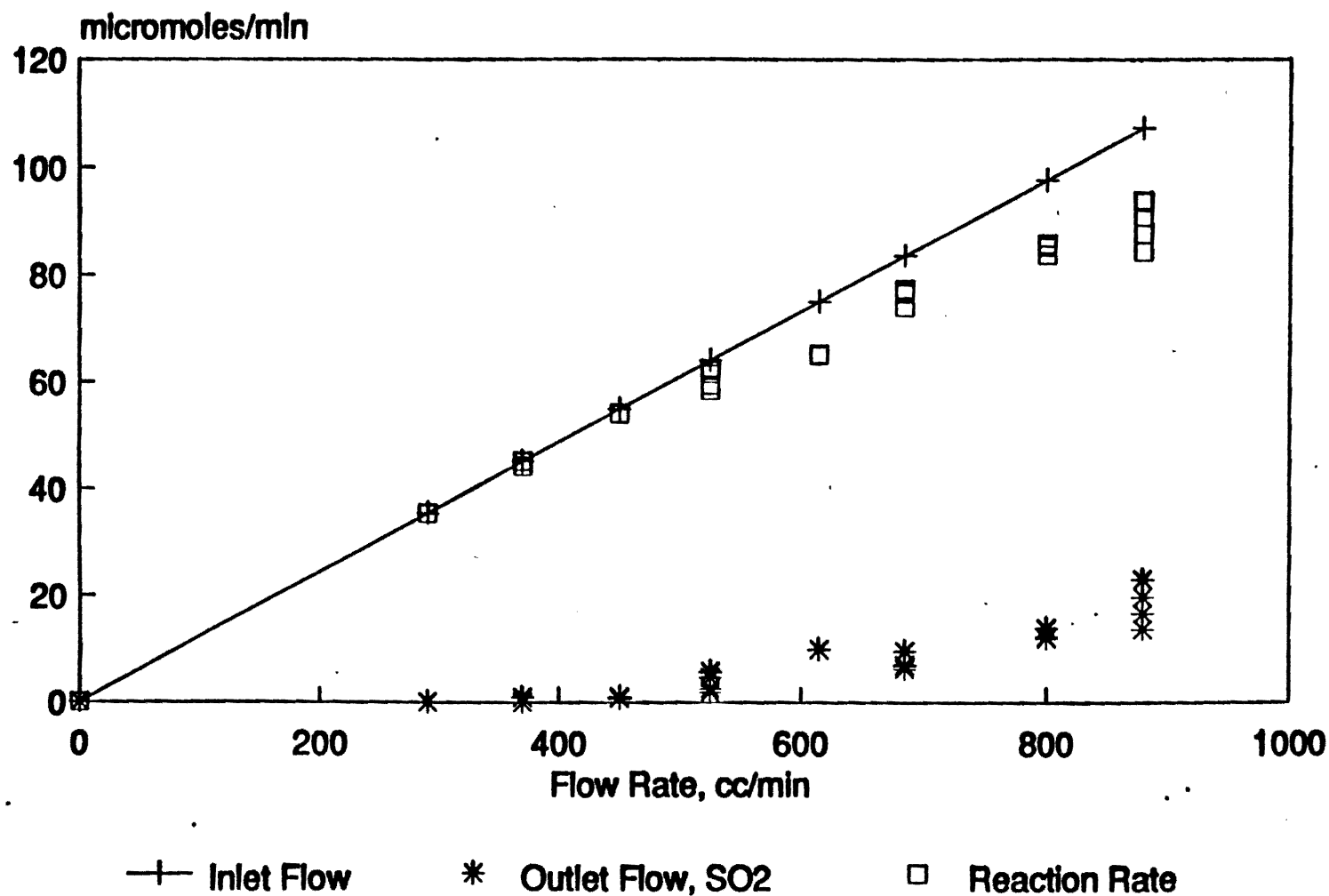
Plots of  $\text{SO}_3$  removal and  $\text{SO}_2$  generation rates versus applied current show that as current increases, removal deviates significantly from stoichiometric levels. Figure 9 shows that  $\text{SO}_3$  removal is approaching a mass transfer limit. The curve for  $\text{SO}_2$  generation accounts for  $\text{SO}_2$  slip through the pre-oxidation catalyst.

The decrease in  $\text{SO}_3$  removal seems to be due to a mass transfer limitation at the electrode. Calculation of the mass transfer of  $\text{SO}_3$  from the gas to the electrode, using a standard correlation for this cell configuration<sup>3</sup>

$$N_{Sh} = \frac{k_m D_{aq}}{D_{AB}} = 5.60 \quad (3)$$

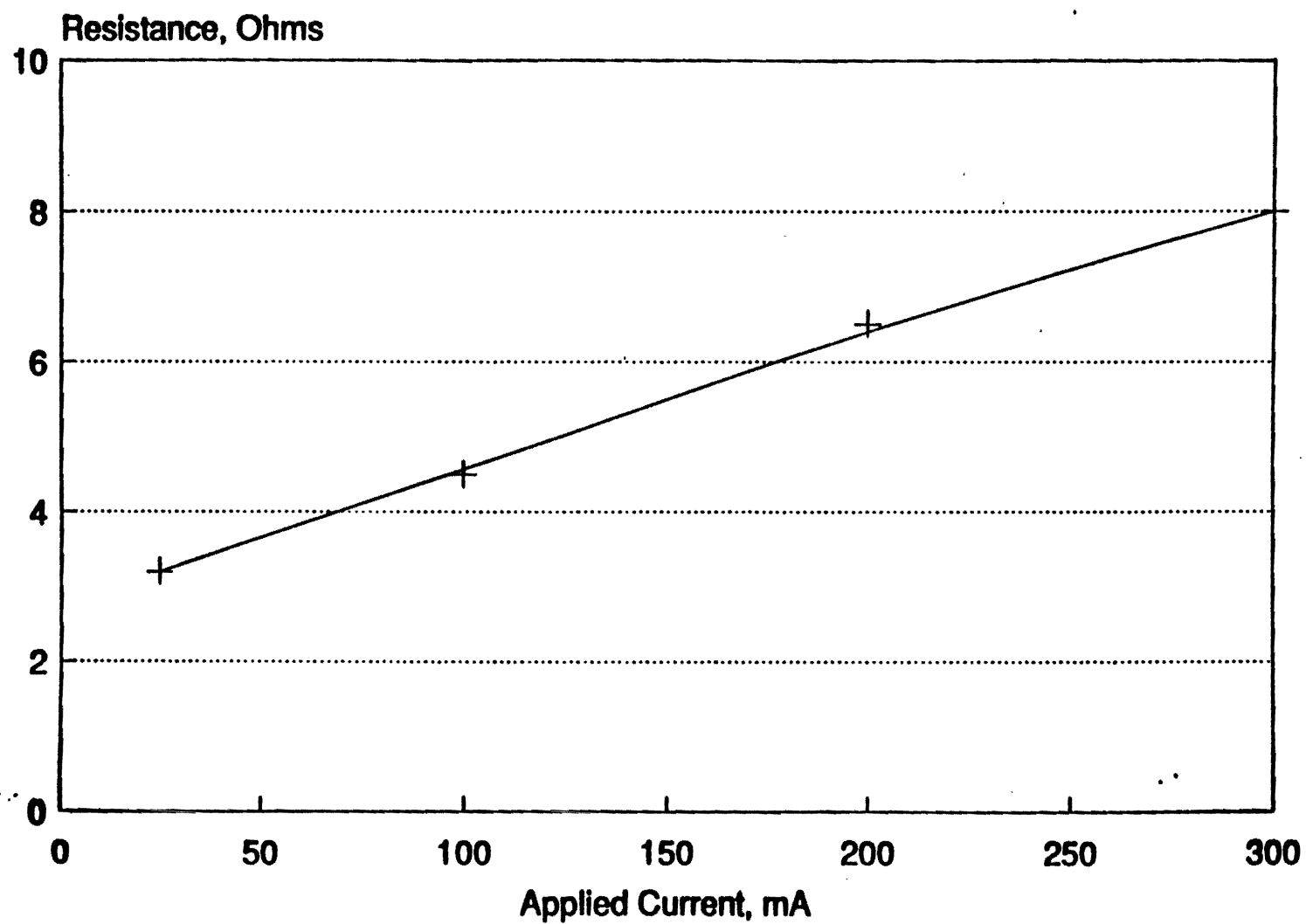
shows that the gas-phase mass transfer limiting current is 50 mA/cm<sup>2</sup>. This value is higher than the maximum applied current of 300 mA (15 mA/cm<sup>2</sup>), superficial area

# SO<sub>2</sub> Bypass

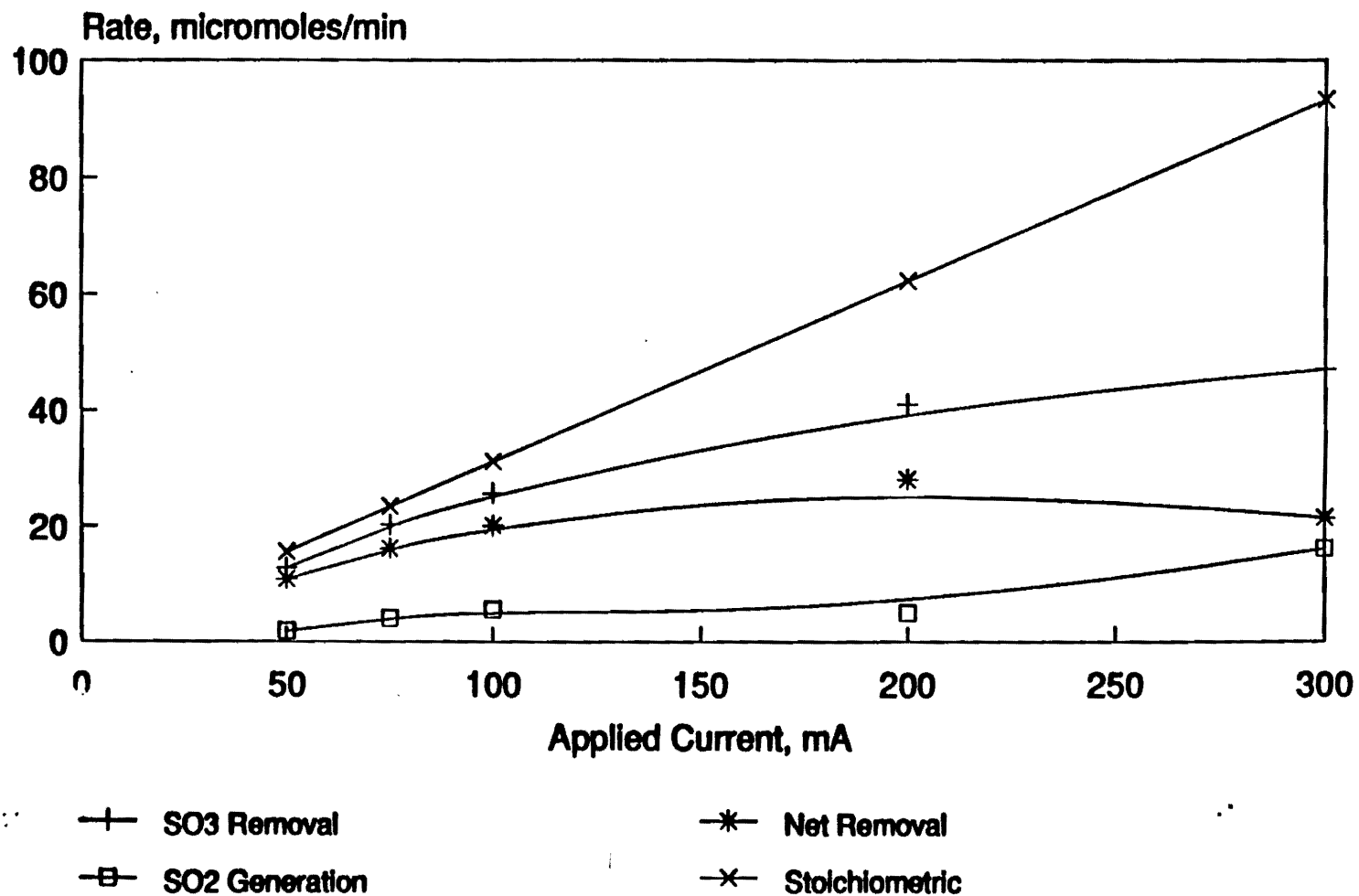


Mass of catalyst = 1.745g

Figure 7. Bypass of SO<sub>2</sub> through pre-oxidation catalyst bed; 400° C; 0.3% SO<sub>2</sub>, 3.0% O<sub>2</sub> in N<sub>2</sub>.



**Figure 8.** Instantaneous ohmic resistance versus applied current, measured from cathode to anode.



**Figure 9.** SO<sub>2</sub> generation and SO<sub>3</sub> removal rates as a function of applied current; 400° C. 0.3% SO<sub>2</sub>, 3.0% O<sub>2</sub> in N<sub>2</sub> at a flow rate such that current equals 90% removal of SO<sub>2</sub>.

basis) and therefore the cell should be able to support these high currents without modification. Some other cause, such as limited transport of sulfate ions to the gas/electrolyte interface, is responsible for the  $\text{SO}_2$  removal limitation.

The increase in  $\text{SO}_2$  generation is due to a combination of factors. First,  $\text{SO}_2$  generation is directly proportional to applied current, but does not follow the same slope in Figure 9. Second, as current increases, so does the gas flow rate, which means any gas escaping the membrane has a lower residence time and therefore lower contact time with the  $\text{V}_2\text{O}_5$  in the electrolyte, however, the slope again does not follow that of the stoichiometric curve in Figure 9. Third,  $\text{V}^{5+}$  in the vanadium complex is reduced by  $\text{SO}_2$  to  $\text{V}^{4+}$ , which has limited solubility in the melt. If this complex is not re-oxidized by gaseous oxygen, precipitation occurs, reducing the amount of catalyst available for  $\text{SO}_2$  oxidation. This appears to be the case with the data.

Calculations of the rates of absorption of  $\text{SO}_2$  and  $\text{O}_2$  into vanadia-pyrosulfate melts and the re-oxidation of  $\text{V}^{4+}$  were performed to see if the melt chemistry is limiting removal performance. The work of Holroyd and Kenney<sup>4</sup> for  $\text{SO}_2$  absorption into films of molten  $\text{V}_2\text{O}_5/\text{K}_2\text{S}_2\text{O}_7$  can be applied to the present process to show that the initial rate of absorption is  $36 \times 10^{-9}$  gmol/cm<sup>2</sup>/min. At 100 mA of current,  $\text{SO}_2$  is electrochemically generated at the rate of  $15.5 \times 10^{-6}$  gmol/min. Complete absorption, assuming total escape of generated  $\text{SO}_2$ , would require a melt surface area of 430 cm<sup>2</sup>, or an electrode surface area enhancement of 21.5. These numbers increase linearly with increasing current. Holroyd and Kenney also investigated the reoxidation of  $\text{V}^{4+}$

in the same melts<sup>5</sup> and found that  $V^{4+}$  has a maximum solubility of 4% at 400° C. From their reaction constants, the rate of reoxidation in this system can be calculated as  $14.5 \times 10^{-6}$  gmol/cm<sup>2</sup>/min for 4%  $V^{4+}$ . With the rate of reoxidation being orders of magnitude faster than the absorption of  $SO_2$ , this step cannot be limiting.

However, Mars and Maessen<sup>6</sup> determined that there was a deviation from their normal kinetic behavior at lower temperatures ( $T < 415^\circ \text{C}$ ) for sulfuric acid catalyst pellets. They attributed this to either an increase in the rate-retarding effect of  $SO_3$  or the formation of sulfovanadates, which would stabilize  $V^{4+}$ , reducing the rate of reoxidation. Both the rate of  $SO_2$  absorption and the rate of reoxidation could be limiting and therefore an experiment will be conducted next quarter to determine the conversion of  $SO_2$  to  $SO_3$  bubbled through molten 10 wt.%  $V_2O_5/K_2S_2O_7$ .

In addition to these runs with sulfur oxides, the cell was also used with NO and  $NO_2$  gas mixtures. The Thermo Electron Model 10  $NO_x$  Analyzer was calibrated with a known concentration of NO and then used to analyze the other gas cylinders. The NO mix used contained 989 ppm NO and 2 ppm  $NO_2$  in  $N_2$ , while the  $NO_2$  mix was 7 ppm NO and 806 ppm  $NO_2$  in  $N_2$ . These gases were passed through the platinized silica gel catalyst and then over the working electrode. Outlet gas was diluted with dry air, analyzed and the reading corrected for dilution effects. Current was applied to the working electrode, either in reducing or oxidizing fashion.

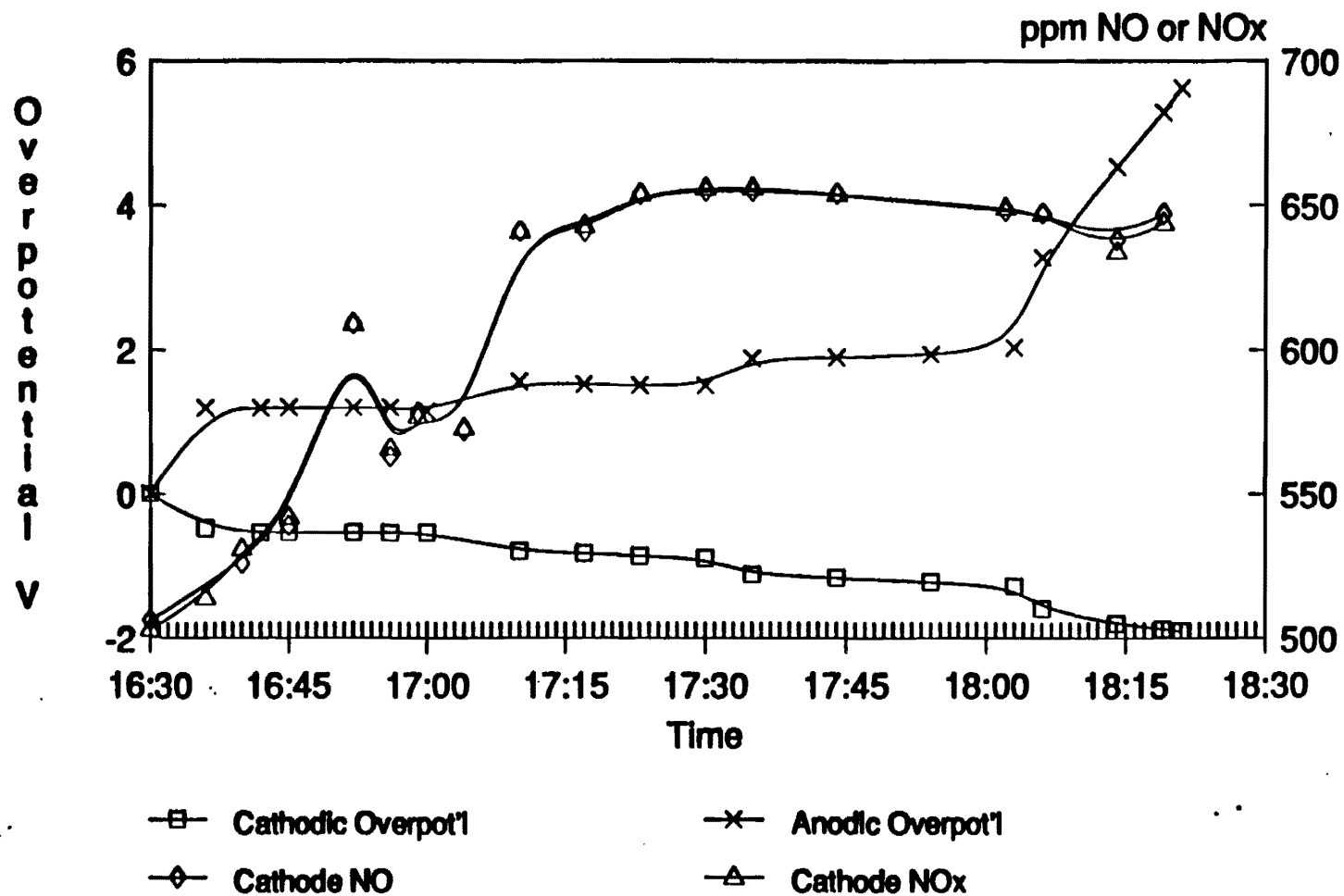
The first NO study used 78 cc/min of  $SO_2$  mix blended with 235 cc/min of NO mix, such that the reduction reactions would have some  $SO_x$  reagent available. However, the gas was set to handle 25 mA, but the current reached levels of 200 mA

to see if NO could be electrochemically reduced also. Figure 10 shows that NO and NO<sub>x</sub> levels increase to a steady-state value of about 660 ppm, with or without reducing current, a removal of 10%. The initial lower concentrations are due to adsorption of NO and NO<sub>2</sub> on the surfaces of the flow system. This trend was confirmed in another run using 233 cc/min NO mix and 78 cc/min SO<sub>2</sub> mix, documented in Figure 11. A similar progression of reducing currents was used with 94 cc/min SO<sub>2</sub> mix and 233 cc/min NO<sub>2</sub> mix, as shown in Figure 12. Again, reducing current had no effect on NO or NO<sub>x</sub> concentrations after adsorption reached equilibrium, with a net removal of 15%.

With oxidizing current applied to the working electrode, little change was seen until the SO<sub>2</sub> mix was turned off. At this time in Figure 13, the NO<sub>x</sub> levels jumped due to a simple concentration effect. When the oxidizing current increased from 200 mA to 500 mA, the NO and NO<sub>x</sub> concentrations dropped immediately to 40 ppm NO and 75 ppm total NO<sub>x</sub>, a removal of 91% of NO<sub>x</sub>. The outlet tubes were cleaned in the middle of this precipitous drop to ensure that removal was due to chemistry, not absorption of NO<sub>x</sub> into condensed SO<sub>3</sub>. After the levels were constant, the polarity of the current was switched to reducing, which caused an immediate increase in NO/NO<sub>x</sub> concentrations. Under these conditions, removal was still 15%.

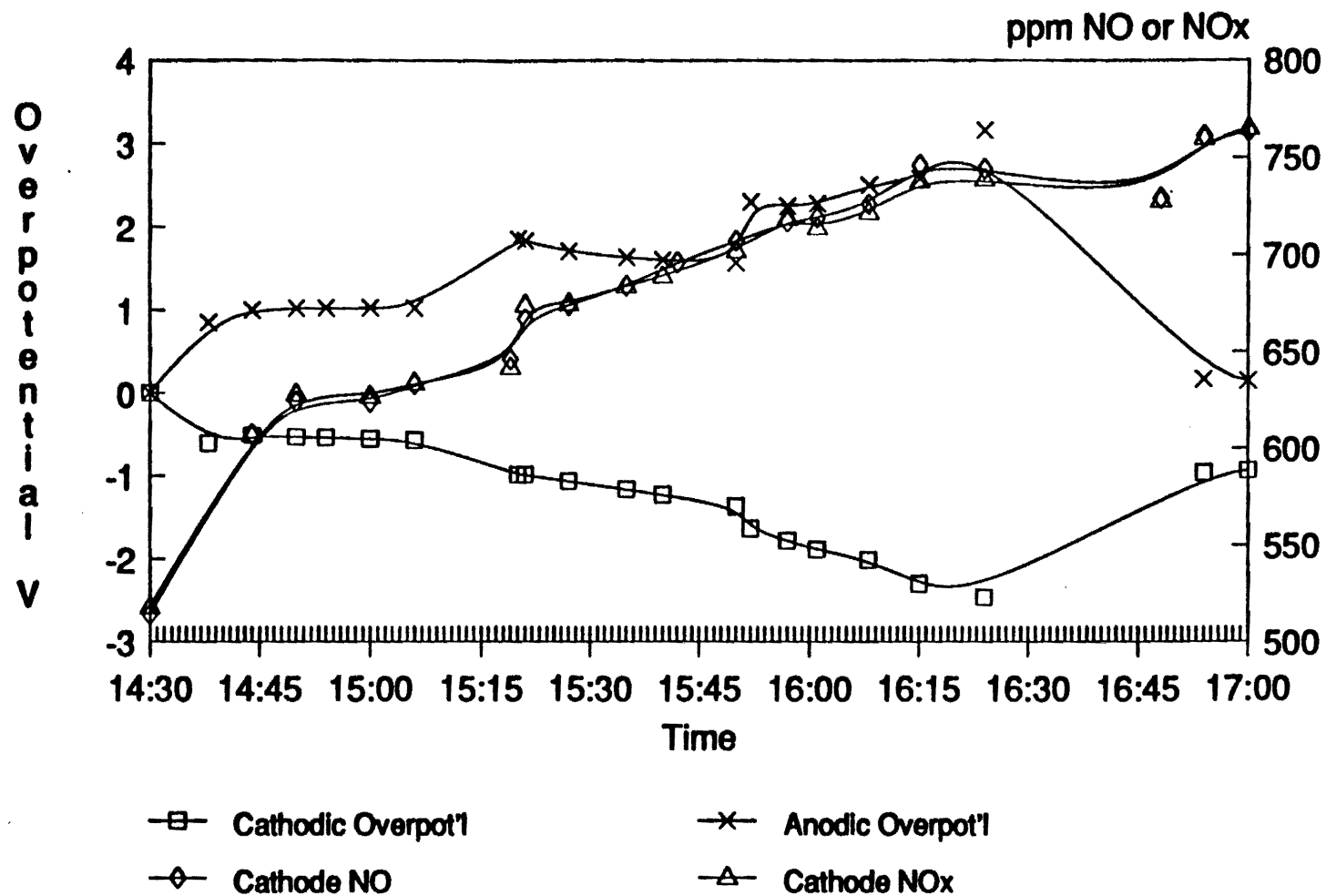
These findings again confirm that the cell has no obvious electrochemical effect on NO or NO<sub>x</sub>. However, all studies showed removal of 10% to 15%, with or without current. When oxidizing current was applied, dramatic decreases in NO and NO<sub>x</sub> concentrations were seen. Previous NO<sub>x</sub> tests have demonstrated 12% removal over





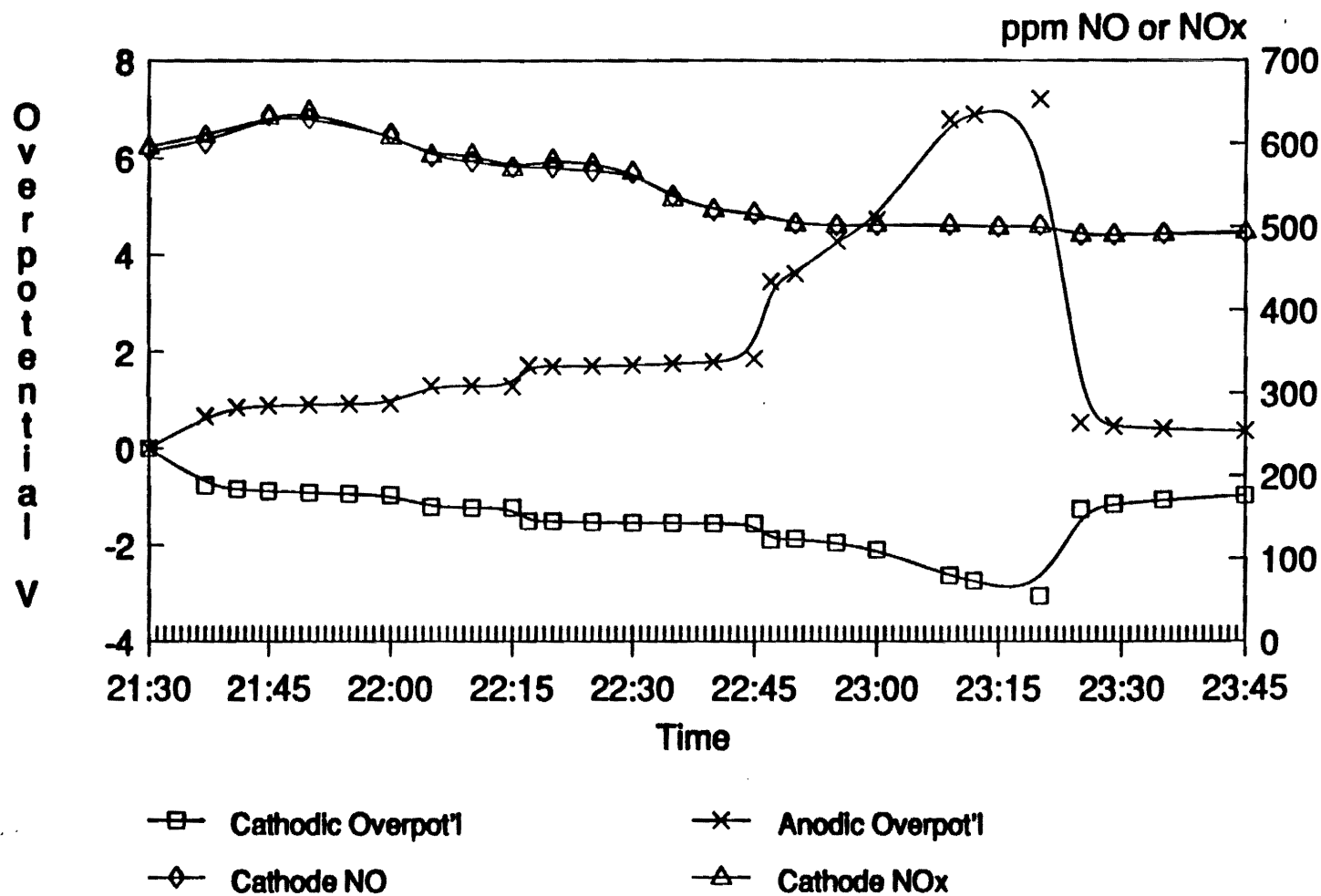
Inlet NO = 742 ppm

**Figure 10.** Overpotentials and NO/NO<sub>x</sub> levels with reducing current and NO mix. Current applied at 25, 50, 100 and 200 mA.



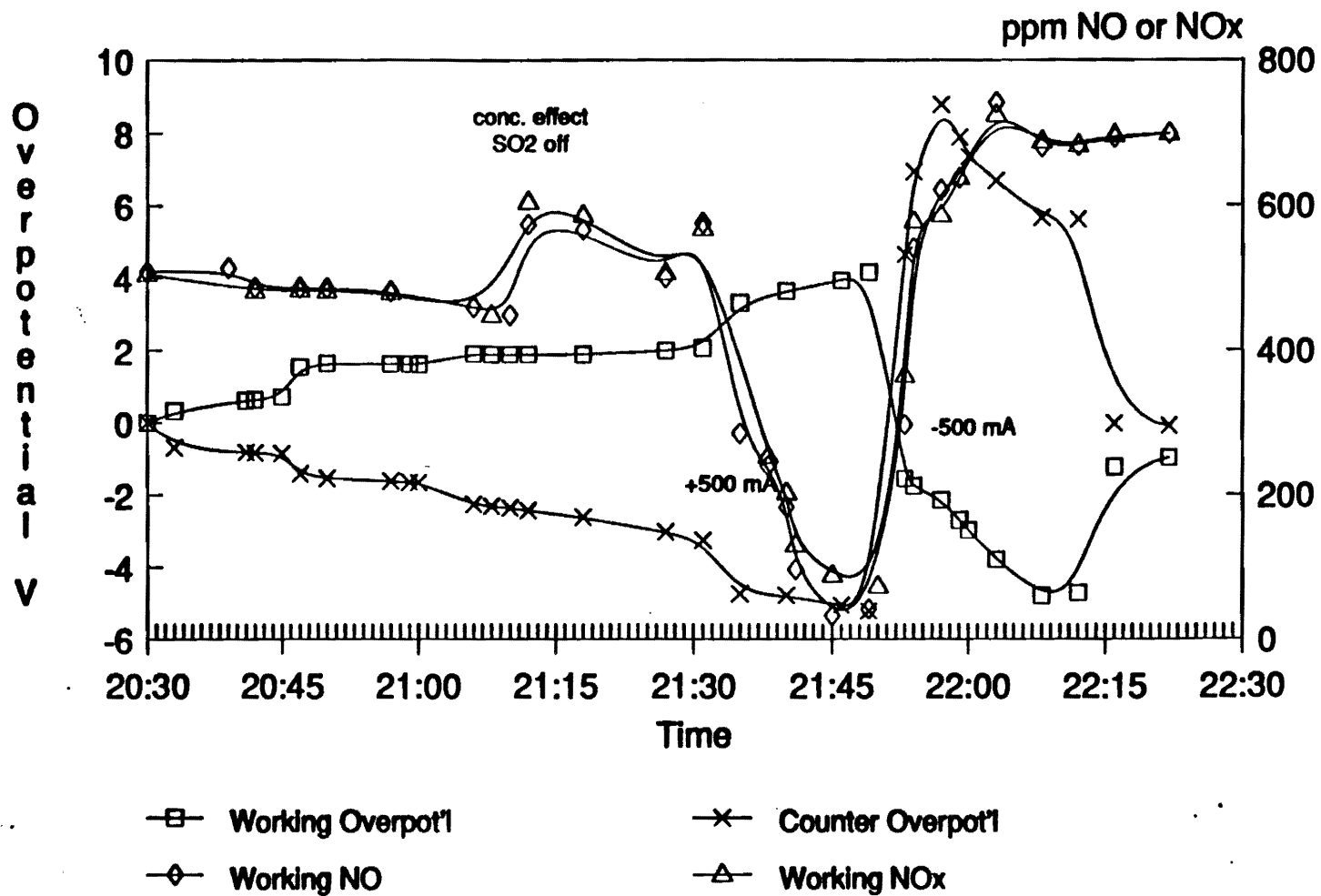
Inlet NO = 745 ppm

**Figure 11.** Overpotentials and NO/NO<sub>x</sub> levels with reducing current and NO mix. Current applied at 25, 100 and 200 mA.



Inlet = 580 ppm NOx

**Figure 12.** Overpotential and NO/NO<sub>x</sub> levels with reducing current and NO<sub>x</sub> mix. Current applied at 25, 50, 100, 200 and 300 mA.



Inlet NO<sub>2</sub> = 600 ppm, then 820 ppm  
**Figure 13.** Overpotentials and NO/NO<sub>x</sub> levels with oxidizing and reducing current.

perovskite electrodes without current.

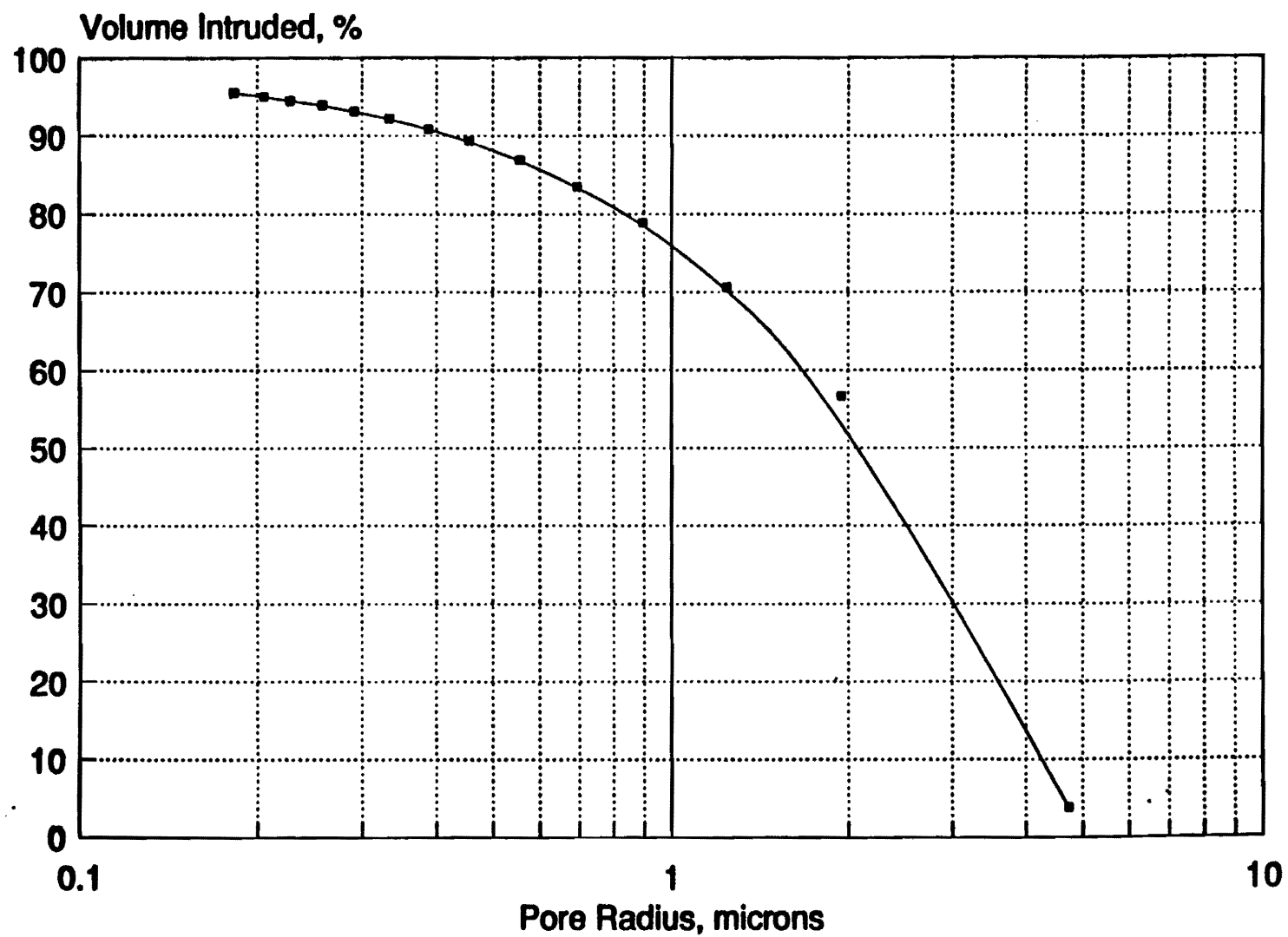
Mercury intrusion porosimetry was performed on the ERC and Fibrex electrode materials. The details of the ERC material are unpublishable due to a secrecy agreement. A plot of volume % v. pore radius, Figure 14, shows that the vast majority (87%) of the pores are greater than 1 micron in diameter ( $r = 0.55\mu$ ). Some of compiled data, Table I, also showed that 57% of the pores were  $\geq 4 \mu$  in diameter, resulting in a good match with the electrolyte membrane structure.

Final experimentation of this quarter included a determination of the feasibility of using commercial sulfuric acid catalyst (Haldor-Topsoe VK38) in the gas channels of the flow cell to convert the electrochemically generated  $\text{SO}_2$  to  $\text{SO}_3$  for removal. A tests was performed using thin cylinders of catalyst trimmed from 6 mm x 6mm catalyst pellets. This test showed a mass transfer limitation to the reaction rate (the horizontal asymptote in Figure 15) with a maximum rate of  $10 \times 10^{-6}$  moles  $\text{SO}_2/\text{min}$  or  $30 \times 10^{-6}$  moles  $\text{SO}_2/\text{min/g}$  catalyst at  $400^\circ \text{C}$ . At  $375^\circ \text{C}$ , this reaction was 5% slower, Figure 16.

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1. Franke, M. and Winnick, J., *I&EC Res.*, **28**, 1352, 1989.
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3. Incropera and DeWitt, Fundamentals of Heat and Mass Transfer, 2<sup>nd</sup> ed., Wiley, NY, 1985.
4. Holroyd, F. P. B. and Kenney, C. N., *Chem. Eng. Sci.*, **26**, 1963, 1971.
5. Holroyd, F. P. B. and Kenney, C. N., *Chem. Eng. Sci.*, **26**, 1971, 1971.
6. Mars, P. and Maessen, J. G. H., *J. Catalysis*, **10**, 2, 1968.

# Partial data

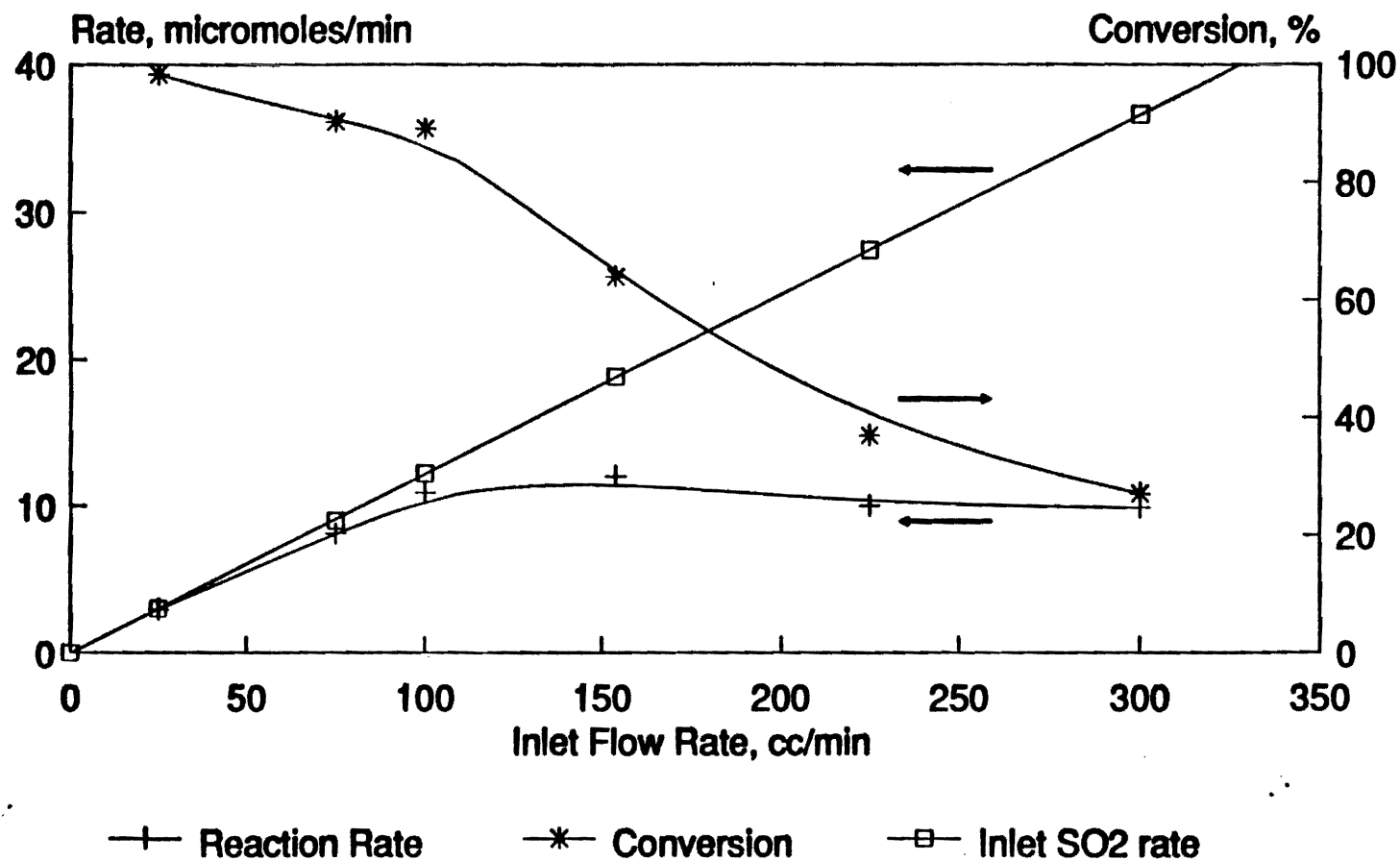


**Figure 14. Mercury Porosimetry Curve for Lithiated and Oxidized Fibrex 50/50 mat.**

**Table I. Data for Mercury Porosimetry of Fibrex 50/50 mat.**

Pore Radius, $\mu\text{m}$	Pore Diameter, $\mu\text{m}$	Intruded Volume, cc/g	% Volume Intruded
4.727	9.454	0.0139	3.8
1.947	3.894	0.2069	56.63
1.241	2.482	0.2579	70.58
0.8944	1.7888	0.2883	78.89
0.6942	1.3884	0.3052	83.52
0.5546	1.1092	0.3177	86.93
0.4554	0.9108	0.3264	89.33
0.3878	0.7756	0.3319	90.84

# SO<sub>2</sub> Reaction Rate for VK38 Pellets in Flow Channels; 400C

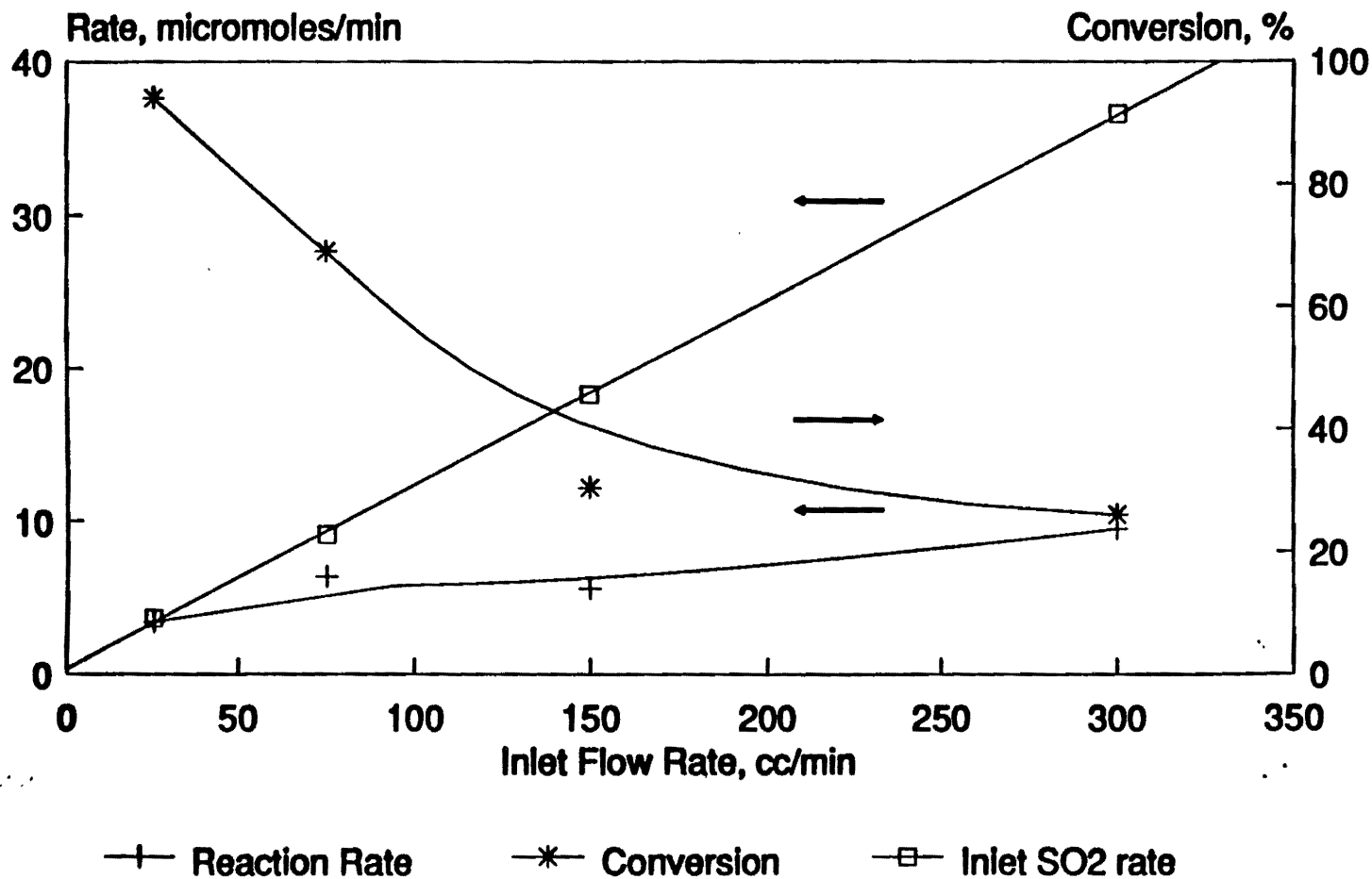


0.358 g VK38 (thin cylinders)

**Figure 15.** Rate and percent conversion of SO<sub>2</sub> over thin cylinders of VK38 catalyst at 400° C.



# SO<sub>2</sub> Reaction Rate for VK38 Pellets in Flow Channels; 375C



0.358 g VK38 (thin cylinders)

**Figure 16.** Rate and percent conversion of SO<sub>2</sub> over thin cylinders of VK38 catalyst at 375° C.

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**Quarterly Progress Report:**  
**High Temperature Membranes for**  
**H<sub>2</sub>S and SO<sub>2</sub> Separations**  
**Grant DE-FG22-90PC90293**  
**January 1, 1992 - March 31, 1992**

by

**Professor Jack Winnick**  
**Georgia Institute of Technology**  
**School of Chemical Engineering**  
**Atlanta, Georgia 30332-0100**

## **Purpose and Goals of Research**

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  cell and the  $\text{SO}_2$  cell require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.

## **I. H<sub>2</sub>S Removal Cell**

### **Introduction**

This electrochemical removal cell cleans a product gas of H<sub>2</sub>S by electronating the most easily reduced component of the stream. In coal synthesis gas or natural gas, this is H<sub>2</sub>S:



A membrane which contains sulfide ions in a molten state will act to transport sulfide across to the anode. If the membrane is capable of preventing diffusion of hydrogen from the cathode side, an inert sweep gas such as N<sub>2</sub> can be used at the anode to carry away oxidized sulfide ions as vaporous S<sub>2</sub>:



### **Research Summary**

The process has been successfully applied to the polishing of H<sub>2</sub>S from simulated coal gasification streams. Removal of H<sub>2</sub>S was shown at 700°C and flow rates varying from 88 cc/min to 600 cc/min. The maximum removal recorded was 89.1% (89.5 ppm to 9.7 ppm). Work has continued using type 316 stainless steel as a housing material and some marginal success has been shown.

## **Experimental Run Results**

### **Run 49**

This was the fifth experimental run using coal gas. It used two tapes of MgO and one mat of zirconia cloth as the membrane matrix material. The electrodes were both lithiated NiO. The acrylic binders in the tapes of MgO were burned out under an O<sub>2</sub> atmosphere and the Li/K eutectic-composition electrolyte was added with the cell at run temperature. MACOR machinable ceramic housings were used instead of stainless steel housings. The inlet gases were passed through a stainless steel shift reactor to allow them to come to their equilibrium composition before passing through the cell.

This experimental run was divided into three sections: the first confirmed ionic transport through the membrane by removal of CO<sub>2</sub> (and H<sub>2</sub>O) from the syn-gas at 625°C (Run 49A), the second was an attempt at removal of H<sub>2</sub>S from the syn-gas at 625°C (run 49B), and the third was an attempt at removal of H<sub>2</sub>S from the syn-gas at 700°C (Run 49C). The results of these studies are presented below:

#### ***Run 49A***

CO<sub>2</sub> removal from the process gas as a function of applied current was recorded and is presented in Table 1. Examination of this data shows that the removal of CO<sub>2</sub> from the cathode side of the cell and production of CO<sub>2</sub> at the anode side of the cell is stoichiometric across the range of applied currents examined.

Fuel gas flow was set at 75 cc/min and N<sub>2</sub> sweep was set at 63 cc/min. Seals were good and no cross-flow between the two process streams was observed.

**Table 1.**  
**Run 49A Recorded Data.**

<u>Applied Current (mA)</u>	<u>Actual Cathode CO<sub>2</sub> Out</u>	<u>Calc. Cathode CO<sub>2</sub> Out</u>	<u>Actual Anode CO<sub>2</sub> Out</u>	<u>Calc. Anode CO<sub>2</sub> Out</u>
0	17.8%	17.8%	0.0%	0.0%
100	16.8%	16.8%	1.8%	1.2%
200	15.8%	15.7%	2.8%	2.4%
300	15.2%	14.7%	3.8%	3.7%

This data shows that the cell was functioning properly with respect to ionic transport of carbonate through the electrolyte.

After 2.65 hours with current applied, cross-flow between the cathode and the anode was observed, indicating that the ceramic matrix was damaged. Over the next 13.25 hours, 10.5 grams of electrolyte were added to the cell in order to stop this cross-flow by flooding any matrix cracks with electrolyte. Cross-flow between the two process streams was stopped in this manner and H<sub>2</sub>S removal with applied current was then examined.

#### *Run 49B*

After 22.3 hours exposure to fuel gas at 625°C, an exit H<sub>2</sub>S composition of 27.7 ppm was recorded. A current of 5 mA was applied to the cell (0.63 mA/cm<sup>2</sup>, superficial electrode area = 7.92 cm<sup>2</sup>). After 27.7 hours with applied current, no

significant removal of  $\text{H}_2\text{S}$  was observed. Examination of the limiting current densities at these run conditions shows that at  $625^\circ\text{C}$  the gas phase limiting current density is only  $1.1 \text{ mA/cm}^2$  while the membrane limiting current density is only  $1.4 \text{ mA/cm}^2$ . This membrane limiting current density assumes an electrolyte diffusivity of  $10^{-5} \text{ cm}^2/\text{sec}$ . Once membrane porosity and tortuosity are taken into account, this estimate is in all probability too large. As an 'order-of-magnitude' estimate, however, it does show that the transport through the membrane is on the same order as the transport through the gas phase. It is probable that at these temperatures, the membrane cannot support the necessary flux of sulfide ion to significantly affect the exit  $\text{H}_2\text{S}$  concentration. Further study at these temperatures is required before this statement can be made with confidence.

#### *Run 49C*

Cell temperature was increased to  $700^\circ\text{C}$ . At this temperature, analysis of limiting current densities within the system shows that the gas phase limiting current density is  $1.15 \text{ mA/cm}^2$  while the membrane limiting current density is  $3.29 \text{ mA/cm}^2$ . This shows that even if the electrolyte diffusivity estimate is in error, the membrane flux is three times greater at this temperature than at  $625^\circ\text{C}$ .  $\text{H}_2\text{S}$  removal at a variety of flowrates was observed and is tabulated in Table 2. The overpotentials reported here have not been corrected for IR loss. The measured cross-cell resistance by current interrupt was observed to be only around  $1\Omega$ . With the maximum current applied to the cell only  $20 \text{ mA}$ , this corresponds to only  $20 \text{ mV}$  of



ohmic loss. This is negligible compared to the overall cross-cell potential, which includes concentration effects, and potentials required to drive the electrochemical reactions.

**Table 2.**  
**Run 49C Recorded Data.**

<u>Time</u>	<u>Applied Current (mA)</u>	<u>Cathode H<sub>2</sub>S Out (ppm)</u>	<u>Cathode - Reference Overpotential</u>	<u>Anode - Reference Overpotential</u>
Cathode flow = 88 cc/min				
17:21 (2/16)	0	85.0	0.0	0.0
18:15	5	26.7	-0.007	0.159
19:48	5	16.0	-0.006	0.127
21:30	0	89.5	0.0	0.0
8:46 (2/17)	0	89.5	0.0	0.0
10:00	5	20.0	-0.030	0.149
12:02	1.2	42.0	N/A	N/A
12:35	2	51.5	-0.017	0.030
13:00	2	47.5	N/A	N/A
13:15	2	53.0	N/A	N/A
13:34	20	29.5	N/A	N/A
14:20	20	9.7	N/A	N/A
14:47	15	18.5	-0.023	0.099
15:07	10	25	-0.022	0.050
15:48	20	15.5	-0.033	0.106
Cathode Flow = 210 cc/min				
17:10	0	57	0.0	0.0
18:05	5	35.5	-0.014	0.127
19:00	5	30.6	N/A	N/A
20:09	10	31.5	-0.008	0.213
10:51 (2/18)	0	75.5	0.0	0.0
11:34	5	38.5	0.0	0.184
12:01	5	32	0.003	0.253
12:58	5	30	0.011	0.280
14:23	5	28.5	0.017	0.299

**Table 2 (con.)**  
**Run 49C Recorded Data.**

<u>Time</u>	<u>Applied Current (mA)</u>	<u>Cathode H<sub>2</sub>S Out (ppm)</u>	<u>Cathode - Reference Overpotential</u>	<u>Anode - Reference Overpotential</u>
Cathode Flow = 400 cc/min				
21:15	0	59.4	0.0	0.0
21:40	5	48.7	-0.093	0.004
21:55	5	44.5	-0.088	0.055
22:24	5	39.7	-0.081	0.099
22:48	5	39.7	-0.082	0.117
10:31 (2/19)	0	73	0.0	0.0
14:14	10	49	-0.007	0.150
14:55	10	37.3	0.002	0.280
15:34	10	38	0.007	0.293
16:16	15	37.5	0.009	0.333
17:08	15	38.3	0.014	0.343
17:55	20	38.7	0.012	0.326
Cathode Flow = 600 cc/min				
12:00 (2/20)	0	68	0.0	0.0
12:44	10	42	-0.001	0.208
13:15	10	43.3	0.0	0.273
13:45	10	48.3	0.006	0.249
14:30	20	46	0.001	0.318
15:00	20	40	0.003	0.310
15:30	20	45.3	0.003	0.365

The above data are presented graphically in Figures 1 through 4. The H<sub>2</sub>S exit composition is plotted against run event for the 88 cc/min data in Figure 1. Note that initially, the membrane was showing process stream cross-flow. 1.5 grams of electrolyte were added to stop the cross flow and 5 mA were applied to the cell. This current level corresponds to five times the theoretical current required for complete H<sub>2</sub>S removal. After driving the H<sub>2</sub>S down to 16 ppm (81.2% removal, zero current

basis) the current was turned off. The exit  $\text{H}_2\text{S}$  level returned to 89.5 ppm. The lowest level to which the  $\text{H}_2\text{S}$  level was driven was 9.7 ppm (89.1% removal, zero current basis). This data shows good response of the system to applied current. The overpotential to accomplish this removal is shown by Figure 5 to be negligible.

The  $\text{H}_2\text{S}$  removal versus run event for the 210 cc/min data is shown in Figure 2. This data still shows good response of the system to applied current. More electrolyte had to be added to repair membrane damage, and thus the initial exit  $\text{H}_2\text{S}$  cathode level with no current applied is down to 57 ppm. This is due to a build-up of carbonate caused by excess electrolyte which had been added to the system.

The data taken at a flowrate of 400 cc/min is presented in Figure 3 and the data taken at 600 cc/min is presented in Figure 4. Comparison of this data with the overpotential results presented in Figure 5 shows that the efficiency of the system dropped off with time. At several points through the run, as marked on Figures 1 through 4, electrolyte was added to stop cross-over between the cathode side of the cell and the anode side. The increase in anodic overpotential shows that this excess electrolyte had flooded the anode, thus decreasing the reactive surface area from the interfacial area of the electrolyte wetting the walls of the electrode capillaries to the superficial area of the electrode when the pores were fully flooded. This was verified in the post-mortem analysis of the cell when the assembly was taken apart and the components examined. The anode flooded because it is physically on the bottom of the assembly.

A total of 18.7 grams of electrolyte was added to the membrane during the

course of the run in addition to the 11 grams that were initially added to fill the ceramic matrix of the membrane. Post-mortem examination of the membrane showed a small fracture in the matrix around the edge of the electrodes. This fracture would be temporarily flooded with electrolyte to form a gas impermeable barrier. However, aggressive attack by the electrolyte on the MACOR housings would deplete the membrane of electrolyte and lead to gas cross-flow. This problem can be overcome by the use of stainless steel housings, which are more resistant to electrolyte attack.

The cell was terminated due to flooding of the anode and poor membrane integrity after 216 hours of operation.

#### Run 50

This was the sixth run with coal synthesis gas. The cell housings were 316 stainless steel that had been sputtered with a 20 micron thick Al coating. The electrodes were NiO and the membrane was two tapes of MgO and two mats of ZYW-30A. Binder burnout was at 350°C under an O<sub>2</sub> atmosphere. Once the binder was burned out, N<sub>2</sub> was started to both the cathode and the anode. The cell was heated to a temperature of 700°C. Once the cell was at run temperature, a total of 20 grams of eutectic Li/K carbonate electrolyte was added. Fuel gas was then started to the cathode side of the cell. Since the membrane did not support any back-pressure without cross-over, a total of 8.3 grams more electrolyte was added to the cell. H<sub>2</sub>S was then added to the fuel gas mixture to bring the inlet H<sub>2</sub>S concentration to 60 ppm. 13 hours later, the exit cathode H<sub>2</sub>S level was only 15 ppm with no current

applied to the cell. The membrane damage appeared to be around the electrode wells on the reference electrode side of the cell. This is the area through which the electrolyte is added after heat-up. The density change caused by absorbing the electrolyte could be damaging the membrane. Future runs will use a pressed disk of electrolyte layered into the composite membrane structure.

The cell was shut down 48 hours later due to uncontrollable cross-flow. No useful data was taken, however this was the first run which used the new Teledyne UV H<sub>2</sub>S analysis system. The UV analysis tracked the usual GC results to within a few ppm (usually > 5 ppm difference).

#### Run 51

This run used stainless steel housings that had been painted with 29wt% Al paint. The electrodes both started as lithiated Ni and were allowed to go to NiO in situ. The membrane was two MgO tapes with one mat of ZYW-30A. 10 grams of electrolyte were pressed into a disk and load into the cell with the membrane materials. The cell was heated under an O<sub>2</sub> sweep until the electrolyte melted and then fuel gas was supplied to the cell (temp approx. 500°C). Cell seals were initially good and the cell responded well with respect to CO<sub>3</sub><sup>2-</sup> transport when no H<sub>2</sub>S was in the fuel gas. Cross cell resistance was high (1.4 Ω) so two more grams of electrolyte were added. This excess electrolyte ran out of the membrane and into the anode flow channels where it was carried by the high sweep rate (200 cc/min N<sub>2</sub> flow) into the anode exit tube. Here it froze once it exited the furnace and clogged the anode exit

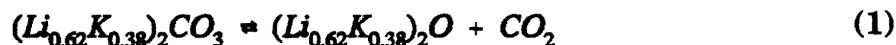
tube. This caused a pressure build-up in the anode side of the cell which ruptured the membrane and shut down the run.

### Run 52

This experimental run used lithiated NiO for both the cathode and the anode. The membrane was two tapes of MgO and two mats of ZYW-30A. The housings were identical to those used in run 51. Sixteen grams of electrolyte were pressed with 20 wt% HEC (hydroxyethyl cellulose) added as a binding agent. This pressed 'green body' of electrolyte was added to the membrane and allowed to heat up with the cell assembly as in run 51. The cell was heated with O<sub>2</sub> supplied to both sides of the cell. The cell was heated to 350°C and the exit CO<sub>2</sub> was monitored to mark the end of the binder burn-out. The cell was then heated to run temperature (700°C) but excess electrolyte once again clogged the exit anode tube. The cell was cooled to 200°C and the anode exit tube was replaced. Once the cell was reheated, no cross-flow was detected. Two hours later, the anode tube once again clogged with electrolyte. The cell was cooled down again and the anode exit tube replaced. The cell was then once again reheated. The membrane seemed to survive this temperature cycling, but the best current efficiency for CO<sub>3</sub><sup>2-</sup> transport that could be observed was only 30%. While the membrane was able to prevent bulk process and sweep gas mixing, enough hydrogen cross-over and CO<sub>2</sub> back diffusion was present to offer no hope for successful H<sub>2</sub>S removal. The cell was therefore shut down.

Run 53

This experimental run used Ni electrodes that were allowed to go to their equilibrium structures in-situ. The membrane matrix consisted of two tapes of MgO layered with two mats of ZYW-30A. The housings were identical to those used in run 52. Since the last run had excess electrolyte present in the initial electrolyte disk, only 13 grams of electrolyte mixed with 20 wt% HEC was pressed and added to this membrane. The cell was heated all the way to run temperature under an O<sub>2</sub> flow on both sides of the cell. The lack of CO<sub>2</sub> in the process or sweep gas caused the electrolyte to decompose by the following reaction:



A thermodynamic analysis of this reaction shows that the equilibrium coefficient of reaction 1 has the form:

$$K_a = \frac{P_{CO_2} a_{(Li_{0.62}K_{0.38})_2O}}{a_{(Li_{0.62}K_{0.38})_2CO_3}}$$

However, since the activities of (Li<sub>0.62</sub>K<sub>0.38</sub>)<sub>2</sub>O and (Li<sub>0.62</sub>K<sub>0.38</sub>)<sub>2</sub>CO<sub>3</sub> are unity in this system, equation 2 reduces to:

$$K_a = P_{CO_2} \quad (3)$$

Thus, by analysis of the system at the run temperature of 700°C, at least 300 ppm CO<sub>2</sub> would have to be present in either the cathode or the anode stream to prevent the decomposition of the electrolyte.

The decomposition of the electrolyte led to matrix failure. The cell was shut

down due to this.

#### run 54

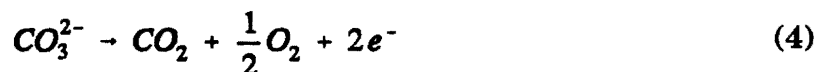
This experimental run was used as a training run for the new graduate student. The housings were identical to those used in run 53. The membrane was two mats of ZYW-30A and two tapes of MgO with a pressed disk of 16 grams of electrolyte with 20 wt% HEC as a binding agent. Leaks in the tubes connecting the manometer across the cathode and the anode sides of the cell lead the student to believe that the membrane had blown and that there was bulk mixing of the process and sweep gas streams since no pressure difference across the membrane could be detected when flow on either side of the cell was throttled. The cell was therefore shut down.

#### Run 55

This experimental run used the same housings as in run 54. The electrodes were both lithiated Ni and were allowed to go to equilibrium composition in-situ. The membrane was two mats of ZYW-30A and two tapes of MgO with 13 grams of electrolyte with 20 wt% HEC pressed into a disk and layered into the initial structure. The cell was heated to 350°C under O<sub>2</sub> and allowed to remain at this temperature for 1 hour. Then fuel gas was started to the cathode side of the cell and N<sub>2</sub> sweep was started to the anode side. This was to prevent electrolyte decomposition as seen in run 53.

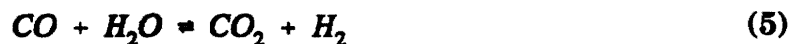


Once the electrolyte had melted, the cell carbonate transport efficiency was measured. Examination of the CO<sub>2</sub> removal showed that cathodic removal efficiency was close to 100% across the range of currents applied to the cell. Examination of CO<sub>2</sub> production at the anode showed that the production efficiency is less than 100% across the range of currents applied. This means that there was an alternative current path present at the anode. Since the housings were acting as the current collectors, if the Al coating on the anode side did not go to a homogenous layer of AlLiO<sub>2</sub> and thus insulate the housing wet seal area, it is possible that electrolyte which had seeped out into the wet seal area was being oxidized:

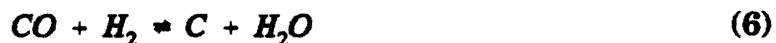


CO<sub>2</sub> from electrolyte oxidized in the wet seal area could escape to the furnace and would not be detected in the anode exit stream.

Once cathodic removal efficiency had been determined, H<sub>2</sub>S was started to the cell at a level of 122 ppm. The cell spent the next four days accumulating enough sulfide in the electrolyte to carry current necessary for H<sub>2</sub>S removal. Some current effect of H<sub>2</sub>S was observed (cathode exit H<sub>2</sub>S level of 35 ppm with no current applied dropping to a level of 28 ppm with 200% stoichiometric current applied). However, the shift reactor, which allows the simulated fuel gas to reach its equilibrium composition through the water/gas shift reaction:



began to clog with carbon. The reverse of the coal gasification reaction could occur at these conditions if the water level in the gas is too low:



It was thought that this reaction was happening before the water/gas shift reaction could build up sufficient water vapor to prevent the carbon monoxide from decomposing to deposit carbon. This problem was solved by hydrating the gas to a level of 3% water vapor (saturated at room temperature) before sending it into the shift reactor. To clear the shift reactor of carbon build up, air was blown through both the cathode and the anode side of the cell until the exit flow rate matched the inlet flow rate and the pressure drop through the shift reactor dropped to only a few mm of H<sub>2</sub>O. Unfortunately, seal integrity was lost on the cathode side of the cell during this process. Seals became so bad that all gas entering the cathode side of the cell was blown into the furnace and no analysis samples could be taken. The seals were lost due to aggressive corrosion on the cathode side of the cell. It is thought that a small leak formed during the carbon clean up process. Gas exiting this leak ignited in the furnace and raised the cell housing temperature locally. This led to an increased local corrosion rate which only led to poorer gas seals and increased leakage. The cell was shut down for this reason.

## Summary

Polishing application of this technology to coal gasification synthesis gas has been demonstrated with  $\text{H}_2\text{S}$  removals as high as 89.1% recorded (Run 49C). Work has proceeded with the stainless steel housings, though no successful runs demonstrating  $\text{H}_2\text{S}$  removal have yet been achieved. However, since stoichiometric  $\text{CO}_2$  removal has been achieved with the stainless steel housings,  $\text{H}_2\text{S}$  removal will not be far behind.

## Planned Work for Next Quarter

Work will continue in the polishing application of this process to coal synthesis gas. Work with the stainless steel housings will also continue. Since the key to successful use of stainless steel housings seems to be insulating the wet seal area to stop carbonate corrosion of the steel and alternative current paths by having the conductive surface of the steel housing in contact with the electrolyte. This will be accomplished by forming an intimately bound layer of Al metal on the wet seal surfaces of the stainless steel housings and then allowing the Al to go to the non-conductive and protective  $\text{LiAlO}_2$  in-situ.

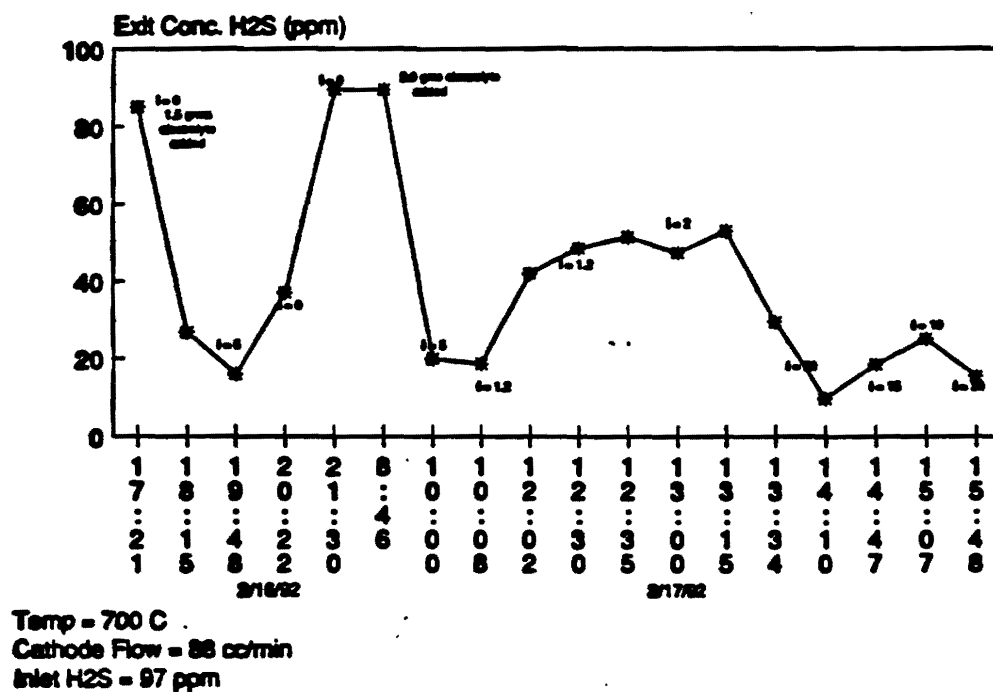


Figure 1.  
H<sub>2</sub>S Concentration vs Applied Current and Time, 88 cc/min, Run 49C.

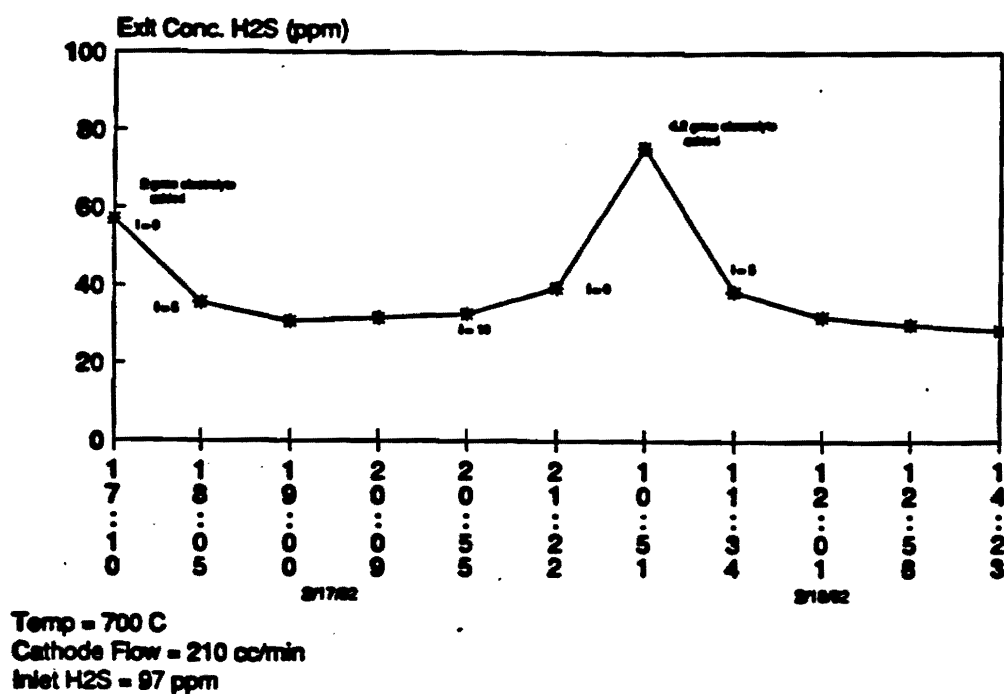


Figure 2.  
H<sub>2</sub>S Level vs Applied Current and Time, 210 cc/min, Run 49C.

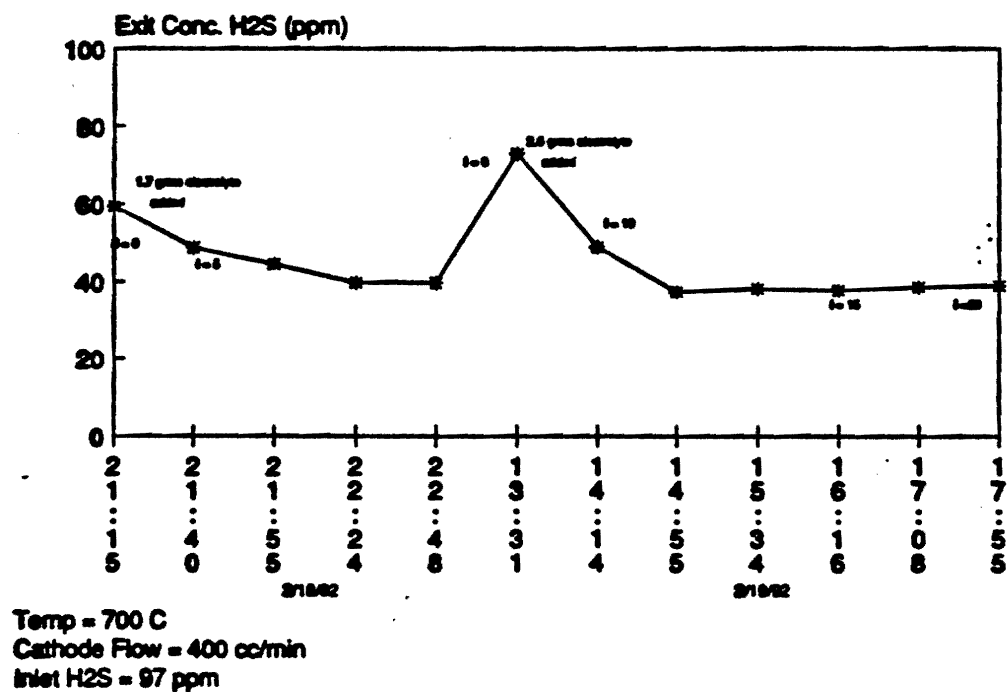


Figure 3.  
H<sub>2</sub>S Concentration vs Applied Current and Time, 400 cc/min, Run 49C.

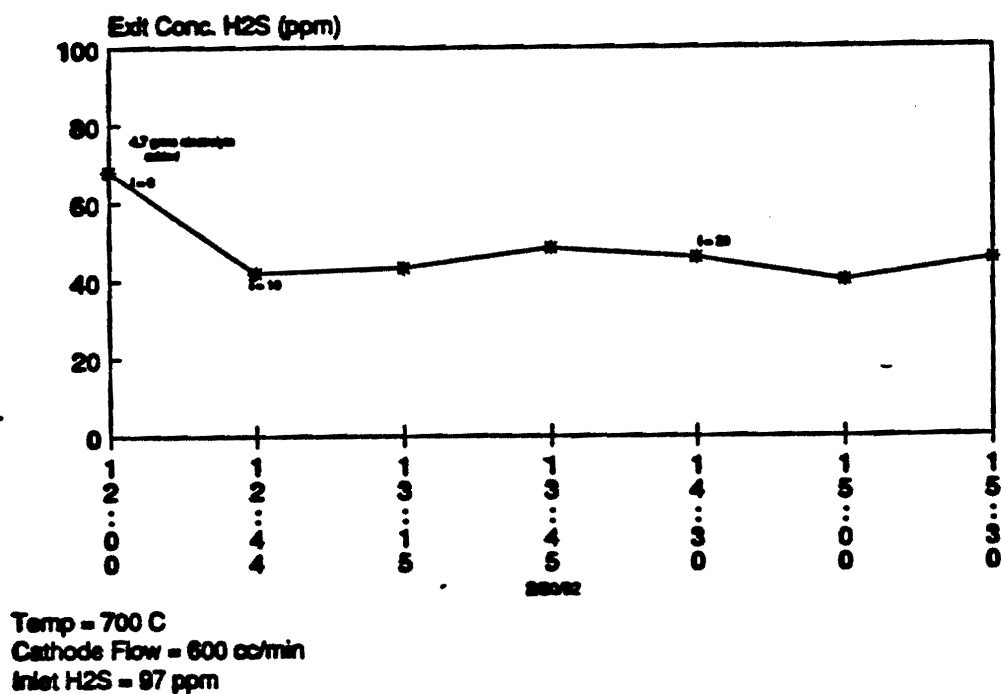
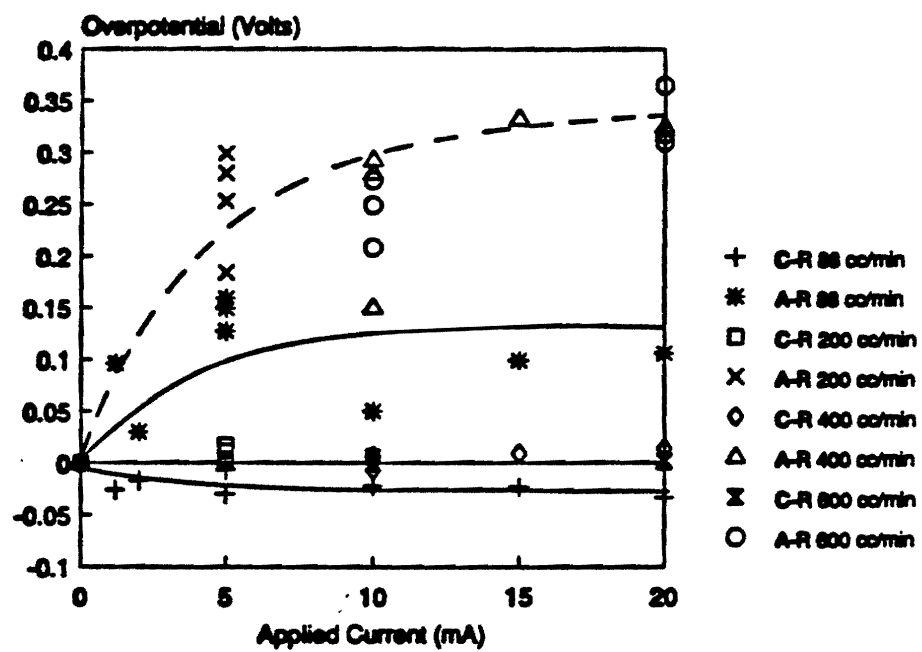


Figure 4.  
H<sub>2</sub>S Concentration vs Applied Current and Time, 600 cc/min, Run 49C.



Temp = 700 C

Figure 5.  
Overpotential vs Applied Current and Time, Various Flow Rates, Run 49C.

## II. SO<sub>x</sub> Removal Cell

### Introduction

The key to the successful application of this removal method is the development of a membrane capable of achieving a current density of 50 mA/cm<sup>2</sup> at total voltages of approximately 1 Volt. Flooding of the electrode pores has been identified as a problem, leading to increased polarizations over time. To reduce flooding, new materials and fabrication methods will be investigated to produce a homogeneous, theoretically dense membrane. The matrix material must have the proper particle size distribution to develop sufficient capillary forces to prevent the electrode from flooding.

The technique used for construction of the ceramic membranes or 'tiles' is tape casting. The matrix material is mixed with an organic binder in a solvent. This mixture is poured at a constant thickness, maintained by an overhead doctor blade. The solvent is then allowed to evaporate, leaving the 'green' tape. This flexible tape is cut to the desired shape and pre-burned: placed in an oven at relatively low temperatures (<170° C), the tape is heated to remove a large amount of the solvent that is present before it is placed into a cell. There is far less organic binder having the possibility of be entrained within the cell as the full scale cell is brought to 400°C. The organic material is burned off in an oxygen atmosphere, leaving the desired rigid body of the porosity needed for the final tile. Electrolyte is then added at operating temperature. Pore size for the matrices used this quarter has been determined to be approximately 0.2µm.

The electrodes are Fibrex Ni sheets, commercially available, cut to a diameter of approximately  $20\text{cm}^2$  area. Before placement into the cell, they are oxidized to NiO, and lithiated to become a p-type semiconductor, in which conductivity increases with temperature. Resistivity at room temperature has been measured at approximately  $2\ \Omega$ . Current travels from the stainless steel housings to the electrode through contact made with the housing. Pore size of the electrodes used this quarter was approximately  $1.0\mu\text{m}$ . The electrolyte is made of a mixture of 10wt%  $\text{V}_2\text{O}_5$  and 90wt%  $\text{K}_2\text{S}_2\text{O}_7$  in all cases. The gas mixture run over the cathode (reducing) side of the cell is composed of 0.3%  $\text{SO}_2$ , 3%  $\text{O}_2$ , and 96.7%  $\text{N}_2$ , except in noted cases, and all  $\text{SO}_2$  is oxidized by platinum pellets to  $\text{SO}_3$  prior to cell entry.

### Research Summary

The production of  $\text{SO}_2$  on the cathode side of the cell has been identified as a problem at high currents. The elimination of this side effect is of paramount interest. Research this quarter centered on the elimination of this  $\text{SO}_2$  production in full scale cell testing. An attempt was also made to introduce the electrolyte into the cell insitu by tape casting. Three full scale tests were done with SS316 housings, at cathodic flowrates of approximately 500 cc/min.

The first run incorporated eleven pellets into the flow channel of the cathode housing. The Haldor Topsoe VK38 pellets are commercially used to oxidize  $\text{SO}_2$  to  $\text{SO}_3$ . They were cut and ground to fit into the flow channels, and attached to the housing with small amount of cement. It was felt that the presence of such a catalyst might reform  $\text{SO}_2$  generated into  $\text{SO}_3$ , allowing the chemical mechanisms of the cell



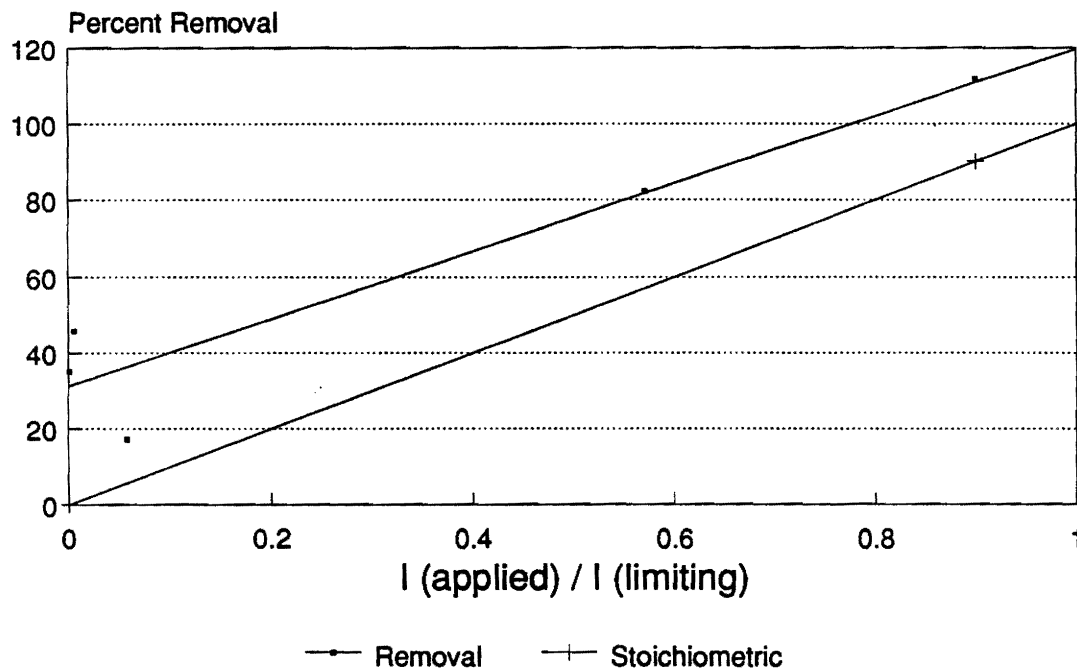
to remove this  $\text{SO}_3$  from the stream.

The run was initiated with  $\text{O}_2$  flow on both sides to facilitate the burnout of the polymer from the ceramic matrix. Upon initiation of the simulated flue gas flow over the cathode side, and a  $\text{N}_2$  purge over the anode, the seal of the matrix was evaluated to be of poor quality, allowing for stream mixing, and poor cell performance. After attempts to revive the test with additional electrolyte failed, the run was terminated. Evaluation upon cooling revealed that the ceramic membrane had been fractured, thereby negating a seal. This cracking was felt to be due to mechanical difficulties rather than chemical or electrochemical. The VK38 pellets were intact and showed little color change.

The second run was of the same type, also incorporating eleven VK38 Haldor Topsoe pellets into the flow channel of the cathode housing. The ceramic matrix thickness was doubled (two tapes were pressed together) in an attempt to prevent mechanical stress fracture. In doing this, no pre-burning of the matrix was possible with the present polyvinyl butyral binder. After three failed attempts to pre-burn the 'green' tape, it was placed directly into the cell with no pre-burn. This may contribute to errors in mass balances due to the organic mixture possibly residing within the cell structure where it cannot be removed.

The cell was run with the simulated flue gas over the cathode side of the cell at a 500 cc/min flowrate, and a pure  $\text{N}_2$  sweep over the anode side of the cell. Removal data at this flow rate can be seen to be higher than that of stoichiometric removal rates in Figure 1. This may be due to the absorption of the gas into the cell

## Removal Data



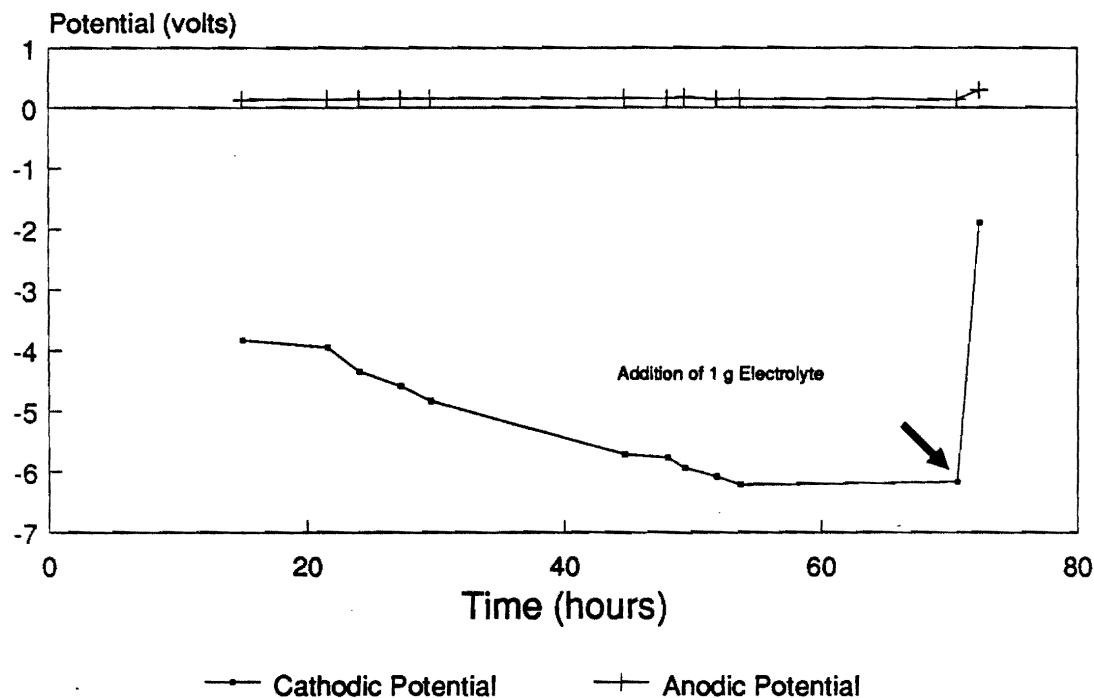
Flowrate= 500 cc/min  
 $I (\text{limiting}) = 196 \text{ mA}$

**Figure 1:** The removal rate for the second run of the quarter.

in an attempt to reach a solubility equilibrium, or to the method of mass flow evaluation. High flow rates have presented a problem in the past, and continue to do so. New methods of evaluation of the mass flows must be developed.

As in the past, it was noticed that the polarity of the cell increased over time as seen in Figure 2, possibly due to the formation of a large, insoluble amount of sulfate at the surface of the electrode. The addition of 1g of electrolyte to the system decreased the polarity of the cell by approximately 65% at virtually constant stoichiometric removal rates. Should the reason for the increased cell polarity be the

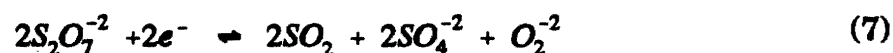
## Time vs. Potential



$I$  (applied) = 100 mA

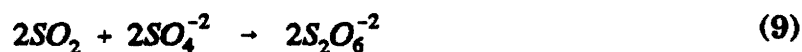
**Figure 2:** The general increase of the polarity of the cell dropped by 65% with the addition of 1g electrolyte.

formation of a layer of sulfate, such a response would be expected, as the addition of the pyrosulfate/pentoxide mixture would tend to dissolve the sulfate formation, and place fresh pyrosulfate at the gas/molten salt/electrode interface.  $\text{SO}_2$  production at the cathode was observed as the total applied current increased.



To evaluate the  $\text{SO}_2$  production at the cathode, the chemistry of the cell need to first be considered on the cathode side. Franke<sup>1</sup> shows the electrochemical

reduction of the pyrosulfate as shown in Equation (7). This reaction must occur at the electrode/electrolyte interface due to the electron transfer required.



$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{x_{SO_2} \gamma_{SO_2}}{P_{SO_2} P_{O_2}} \right) \quad (11)$$

The  $SO_2$  then reacts with the superoxide ion according to Equation (10) and also with sulfate ions present. For the  $SO_2$  to enter the gas stream, it must diffuse through the electrolyte, and into the gas stream. This mass transfer action is in direct opposition to the diffusion of  $SO_3$  from the gas stream to the electrolyte where it reacts. ( $SO_3$  dissolves in the electrolyte, and quickly reacts with the sulfate ion to form the pyrosulfate ion.) Should the superoxide ion not be present (due to the reduction of the vanadium pentoxide) in high enough concentration at the interface, the  $SO_2$  can escape the cell, possibly the cause of the  $SO_2$  production. The overall cathodic cell reaction can be written as seen in Equation (8). The Nerstian potential for this reaction can be written as in Equation (11), where the activity for the gaseous species is approximated as the partial pressure in atmospheres, and the activity of the solvated species is the mole fraction times the activity coefficient.  $E^\circ$  is the standard reversible potential, and  $E$  is the equilibrium potential. It would be

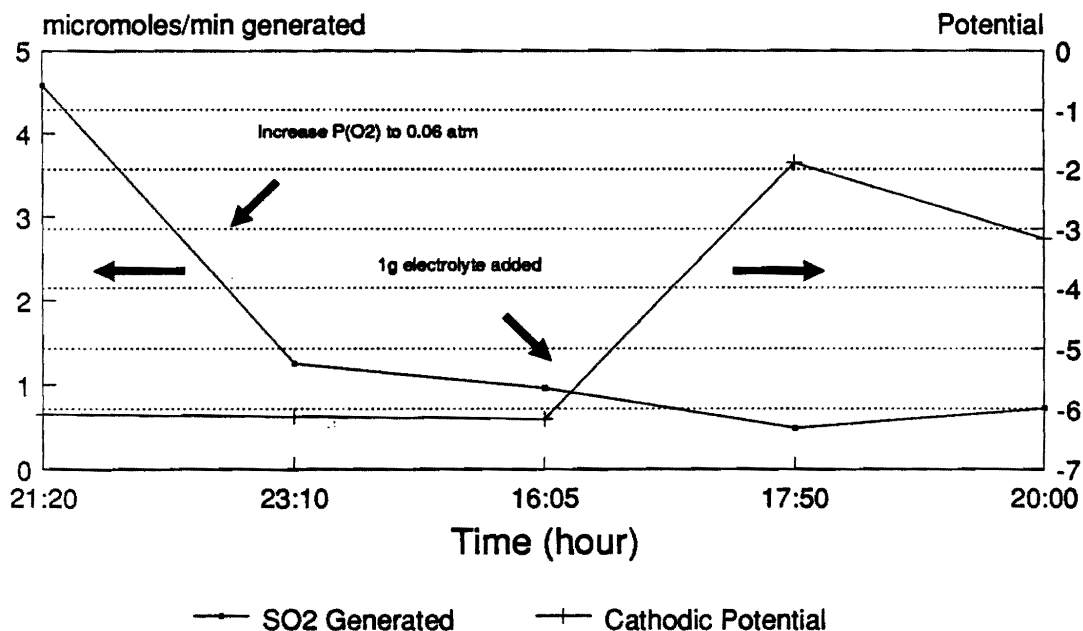
suspected that increasing the partial pressure would have the effect of pushing the equilibrium to the right, thus producing more sulfate ions, reducing the amount of SO<sub>2</sub> production. while lowering the equilibrium potential.



The anodic overall reaction can be written as in Equation (12), so an increase in the dissolved O<sub>2</sub> would increase the reaction resistance unless the availability of the SO<sub>4</sub><sup>-2</sup> is relatively high.

After taking a reading of the cell at 100 mA and a 500 cc/min flowrate, the partial pressure was doubled, and a measure of the SO<sub>2</sub> generation was taken. Figure 4 shows the extrapolated values obtained. It was not known, however, how much of this change in SO<sub>2</sub> generation was due to the electrochemistry of the cell, and how much was due to the oxidation (and possibly increase in activity) of the VK38 pellets in the channel. The cell was then run for an additional 24 hours to determine the long term effects of doubling the O<sub>2</sub> partial pressure, and additional electrolyte was added. Figure 4 shows that the effect of the doubling of the O<sub>2</sub> was effective in reducing the SO<sub>2</sub> generation by 73%, with continuing decrease as time progressed, for a relatively constant cathodic potential of -6.2 Volts. The effect of the addition of electrolyte to the potential has already been established, but the SO<sub>2</sub> generation was again lowered, this time initially by about 50%. As the cathodic potential began to increase, the SO<sub>2</sub> generation also increased. This would suggest that the theory that the formation of the SO<sub>4</sub><sup>-2</sup> on the surface of the electrode over

## SO<sub>2</sub> Generation Under O<sub>2</sub> Pressure Increase Run2



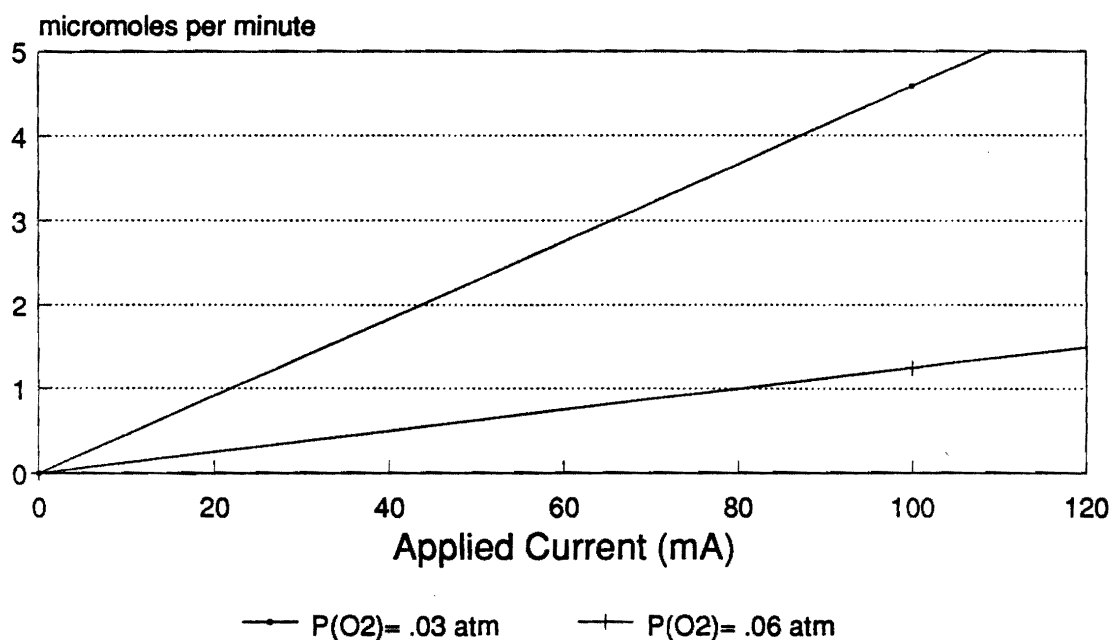
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**Figure 3:** The change in both the cathodic potential and SO<sub>2</sub> generation with the increase in P(O<sub>2</sub>) and the addition of electrolyte.

time might be partially responsible for inability of the electrolyte to internally utilize the SO<sub>2</sub>, as the decreasing surface area available for the dissolving of the O<sub>2</sub> could force the equilibrium in Equation (8) to the right-hand side in a perpetuating cycle.

Upon breakdown, the relative color of the VK38 pellets in the channel showed a change in color only for the pellets nearest the exit, suggesting that any in-channel conversion of SO<sub>2</sub> to SO<sub>3</sub> was taking place primarily at the exit, at approximately 0.36 micromoles/min based on one pellet. However, the change due to the partial pressure of O<sub>2</sub> present was not known. It was therefore determined that a full-scale cell test

## SO<sub>2</sub> Generation Run 2



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**Figure 4:** The extrapolated SO<sub>2</sub> generation for Run 2 with a change in the partial pressure of O<sub>2</sub> from .03 atm to .06 atm.

should be implemented without the VK38 pellets in the flow channels.

Incorporated into this third test which is currently ongoing, was a 'green' tape of electrolyte, placed below the ceramic tape, for the efficient introduction of the electrolyte into the cell. This tape was made with the electrolyte comprising 78% by volume of the mixture (versus the usual 50 vol% in matrix tape-casting). The high percentage insured the a high density of electrolyte, and therefore a thinner tape to wet the matrix and pores of the electrodes. In addition, the high percentage of electrolyte minimized the amount of solid left residually by the binder in the burnout

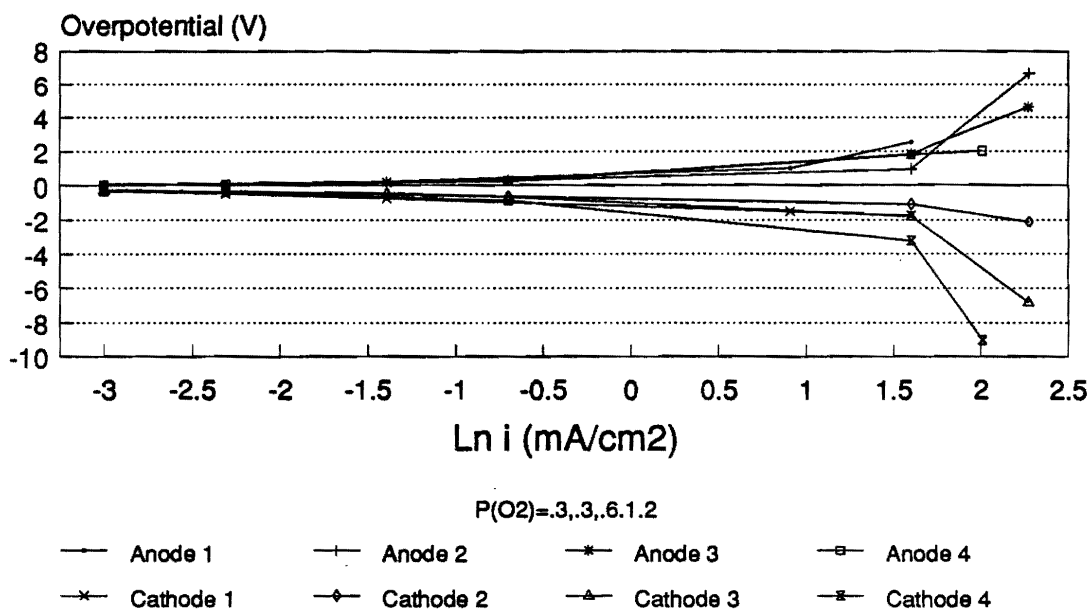
process. The mixture turned out to be problematic, and multiple additions of solvent were needed to insure any mixing whatsoever. Additional surfactant was also added due to the tendency of the agglomerate to stick to the mixing vessel. In the actual tape casting procedure, it was difficult to maintain the homogeneity of the mixture, thus resulting in a variety of different tapes being cast from one batch. Tapes obtained varied from a very thin rubbery film to a thick, crumbling tape. The tape placed into the cell comprised of four separate castings: two somewhat flexible tapes, and two thin rubbery tapes, all cut to the cell size and pressed together.

The temperature of the cell was brought up slowly under pure  $O_2$  on both the cathodic and anodic sides in the attempt to insure the full burnout and removal of the organics from the two ceramic and four electrolyte tapes. This may not have been achieved. As the run continued, the wet seal was determined to be virtually perfect, having the ability to withstand large pressure gradients. Furthermore, the mass flow measurements did not converge throughout the experiment, suggesting the absorption or adsorption of the gas into the organic present. Organic was observed in the exit tubes, and was cleaned. This process was to no avail as the mass balances continued to be in error, and more organic material streamed out of the cell. Measurements should therefore be considered relative only to this cell, and not compared against previous data.

Data was evaluated at  $P(O_2)$  of 0.03, 0.06, and 0.12 atm, at flowrates of 500cc/min to 545cc/min. Increases from 500cc/min were due solely to the addition of  $O_2$ . Figure 5 shows a limitation, probably due to mass transfer, on the cathode side



## Tafel Plot for Varying Partial Pressures O<sub>2</sub>



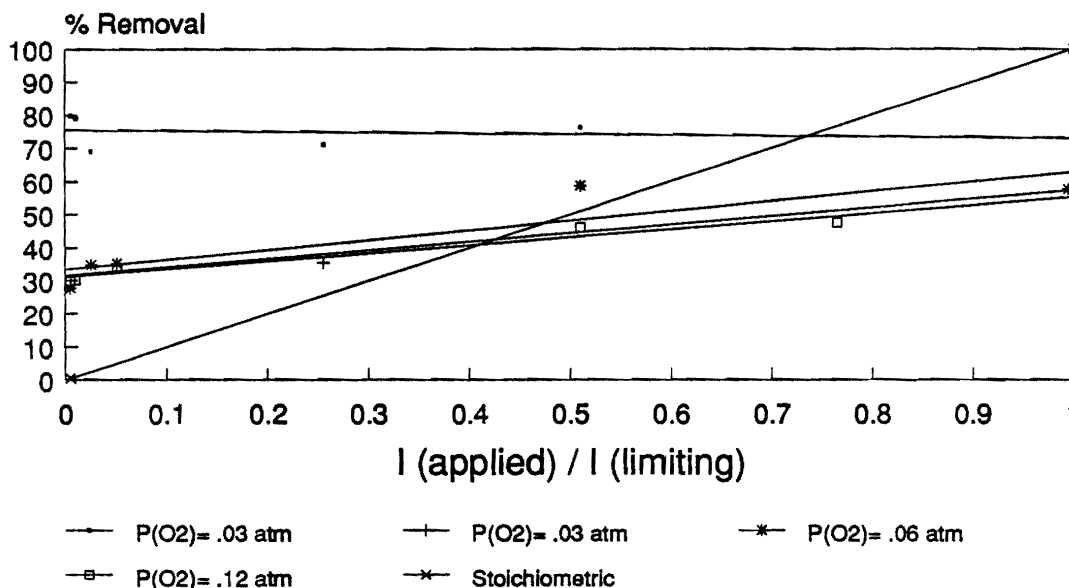
Flowrates = 500cc/min + x%O<sub>2</sub>, ln(i<sub>lim</sub>) = 2.3

**Figure 5:** The variance of Overpotential (Volts) with  $\ln i$  (mA/cm<sup>2</sup>). 1, 2 refers to  $P(\text{O}_2) = 0.03$  atm, 3 to  $P(\text{O}_2) = 0.06$  atm, and 4 to  $P(\text{O}_2) = 0.12$  atm.

increasing with the partial pressure, while the anode shows a decrease in limitations with increasing partial pressure. The data is consistent at low overpotential, leading to an exchange current density ( $i_0$ ) of approximately 1.28 mA/cm<sup>2</sup>. This is an order of magnitude higher than determined by McHenry<sup>2</sup>, but the removal rates obtained are far from stoichiometric as seen in Figure 6. The one varying line was the first data taken, suggesting that an equilibrium had not yet been established.

With the inability of the mass flows to balance, the error involved is substantial. On average, the mass balances were 50% in error. Examination of the

## Applied Current vs. Removal (Based on Cathode SO<sub>x</sub>)

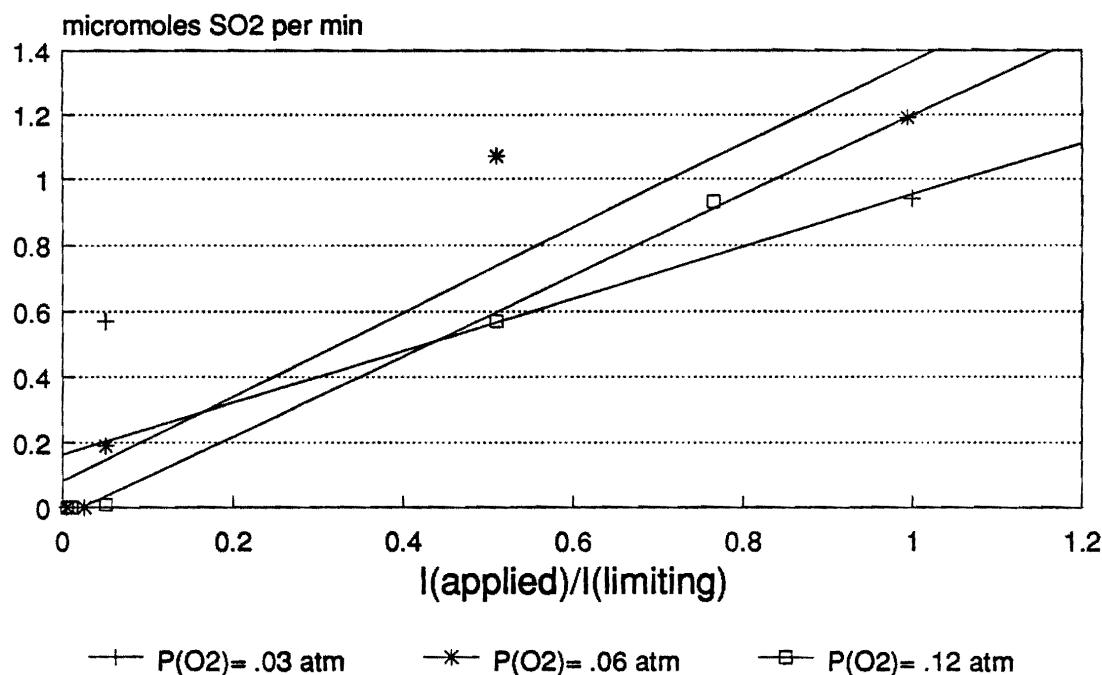


Flowrate = 500 cc/min  
 $I(\text{limiting}) = 196 \text{ mA}$

**Figure 6:** Removal rates based on cathode SO<sub>x</sub> for varying O<sub>2</sub> partial pressures.

rate of SO<sub>2</sub> production shows a definite decrease from a partial pressure of 0.06 atm to 0.12 atm, but, for this same cell, the initial partial pressure of 0.03 has a lower production rate in the high current region, despite a large slope in the low current region (see Figure 7). The error in the mass balances denies any qualitative analysis of the effects of the O<sub>2</sub> partial pressure on the cell. The exceedingly high cell polarizations seen in Figure 5 at high current densities may come from the inability of the cell to remove SO<sub>3</sub> from the cathode stream, thus channeling the current into internal reactions. This inability of the cell to achieve lower SO<sub>2</sub> production may be

# Applied Current vs. SO<sub>2</sub> Production



flowrate= 500 cc/min  
I(limiting)= 195 mA

**Figure 7:** The production variance of SO<sub>2</sub> on the cathode side with various P(O<sub>2</sub>) for a constant flowrate.

due to organics present from the burnout, reducing the surface area available for mass transfer. In addition, the SO<sub>4</sub><sup>2-</sup> formation at the surface may further reduce the available surface area, and lead to further formation of SO<sub>2</sub> over time. The increasing polarization of the cell over time may explaining the conflicting SO<sub>2</sub> production at low partial pressures, as the initial runs were done at low partial pressures, without addition of electrolyte at any point during the run. Testing of this cell is currently ongoing. Further results will be published in future reports.

## Future Testing

As the formation of  $\text{SO}_2$  probably occurs at the electrode/electrolyte interface, the possibility exists of a limitation due to an inadequate surface area. To further increase the surface area, an electrode with smaller pore size will increase the surface area, but will, at this stage be a problem due to capillary action in both the electrodes and matrix. A new matrix will need to be developed to insure the flooding of the matrix while maintaining only a wetted surface in the electrodes.

Further testing and modification of an electrolyte membrane will also be performed. Options for the membrane include changing the binder and solvent, and the volume percent of the electrolyte in such a mixture. The possibility also exists for a cold or hot pressed membrane of electrolyte. A pressed membrane is developed by pressing of loose powdered electrolyte at a pressure of approximately 1200 psi, forming a packed disk of electrolyte. A crumbling disk resulted with the first attempt at this process, possibly due to mechanical shock. A membrane of this type would have no inherent residue, thus reducing any possible reduction of surface area due to organic burnout. Further testing of this process need be done.

Modification of the mass flow analysis needs to be revised. For substantive readings to be taken, the mass balances need to converge close to or at the expected values. A measurement system needs to be developed in which the mass flows can be determined with greater precision and confidence. The high flowrates needed to achieve a current density of  $50 \text{ mA/cm}^2$ , requires the ability to accurately read high mass flows.

1. Franke, M. and Winnick, J., *J. Electroanalytical Chemistry*, **238**, 163, 1987.
2. McHenry, D. J. Development of an Electrochemical Membrane Process for Removal of SO<sub>x</sub>/NO<sub>x</sub> from Flue Gas, Ph. D. Thesis, Georgia Institute of Technology, 1992.

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Quarterly Progress Report:  
High Temperature Membranes for  
H<sub>2</sub>S and SO<sub>2</sub> Separations  
Grant DE-FG22-90PC90293  
April 1, 1992 - June 30, 1992

by

Professor Jack Winnick  
Georgia Institute of Technology  
School of Chemical Engineering  
Atlanta, Georgia 30332-0100



## **Purpose and Goals of Research**

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  cell and the  $\text{SO}_2$  cell require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.

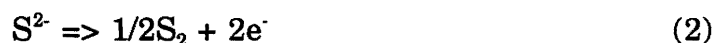
## I. H<sub>2</sub>S Removal Cell

### Introduction

This electrochemical removal cell cleans a product gas of H<sub>2</sub>S by electronating the most easily reduced component of the stream. In coal synthesis gas or natural gas, this is H<sub>2</sub>S:



A membrane which contains sulfide ions in a molten state will act to transport sulfide across to the anode. If the membrane is capable of preventing diffusion of hydrogen from the cathode side, an inert sweep gas such as N<sub>2</sub> can be used at the anode to carry away oxidized sulfide ions as vaporous S<sub>2</sub>:



### Research Summary

Work has continued on application of this technology to polishing H<sub>2</sub>S from simulated coal gasification process streams. Both stainless steel and MACOR housings were successfully used, with 98% (100 ppmv H<sub>2</sub>S to 2 ppmv H<sub>2</sub>S) removal observed at a flow rate of 230 cc/min and a process temperature of 700°C with stainless steel housings (Run 57) and greater than 80% (11 ppmv H<sub>2</sub>S to less than 2 ppmv H<sub>2</sub>S) at a flow rate of 100 cc/min and a temperature of 650°C with MACOR housings (Run 65). Work has continued with attempts to increase removal efficiency by increasing the density of the membrane and slowing down H<sub>2</sub> diffusion from the cathode side to the anode side of the cell.

## A. Experimental Run Results

### Run 56

This experiment used lithiated Ni as both the cathode and the anode of the cell. The membrane was two tapes of MgO suspended within an acrylic binder layered with two mats of zirconia cloth. This was layered with a pressed electrolyte disk which used hydroxyethyl cellulose (HEC) as a binder material. These electrodes and membrane were loaded into a set of new 316 stainless steel housings which were painted with aluminum paint.

The cell was then heated to the binder burnout temperature of 350°C under pure O<sub>2</sub> at a rate of 200°C per hour. Once at the burnout temperature, N<sub>2</sub> was started to the cell and the cell was heated to 420°C. At this temperature, fuel gas (14.5% CO<sub>2</sub>, 46.5% CO, 34.3% H<sub>2</sub>, 6.1% H<sub>2</sub>O, and 106 ppm H<sub>2</sub>S after shift reaction at run temperature of 700°C) was started to the cell and the furnace was heated to 700°C. Under these conditions, the equilibrium sulfide level in the membrane should have been 0.6 mole%. The gas phase limiting current density was calculated as 1.22 Ma/cm<sup>2</sup> and the membrane limiting current density was estimated as 1.87 Ma/cm<sup>2</sup>.

H<sub>2</sub>S removal data (presented in Figure 1) and cross-cell potential data (presented in Figure 2) were recorded. While some H<sub>2</sub>S removal was recorded, current efficiencies were unacceptably low (with stoichiometric current at this concentration and flow rate being only 3 mA applied current). Current efficiency was low due to H<sub>2</sub> cross-over and the presence of a possible alternative current path.

After cell shut-down, carbon build-up between the electrodes in the membrane was observed. This may have been caused by pyrolyzed HEC since this was not observed in runs which did not use HEC as an electrolyte binder.

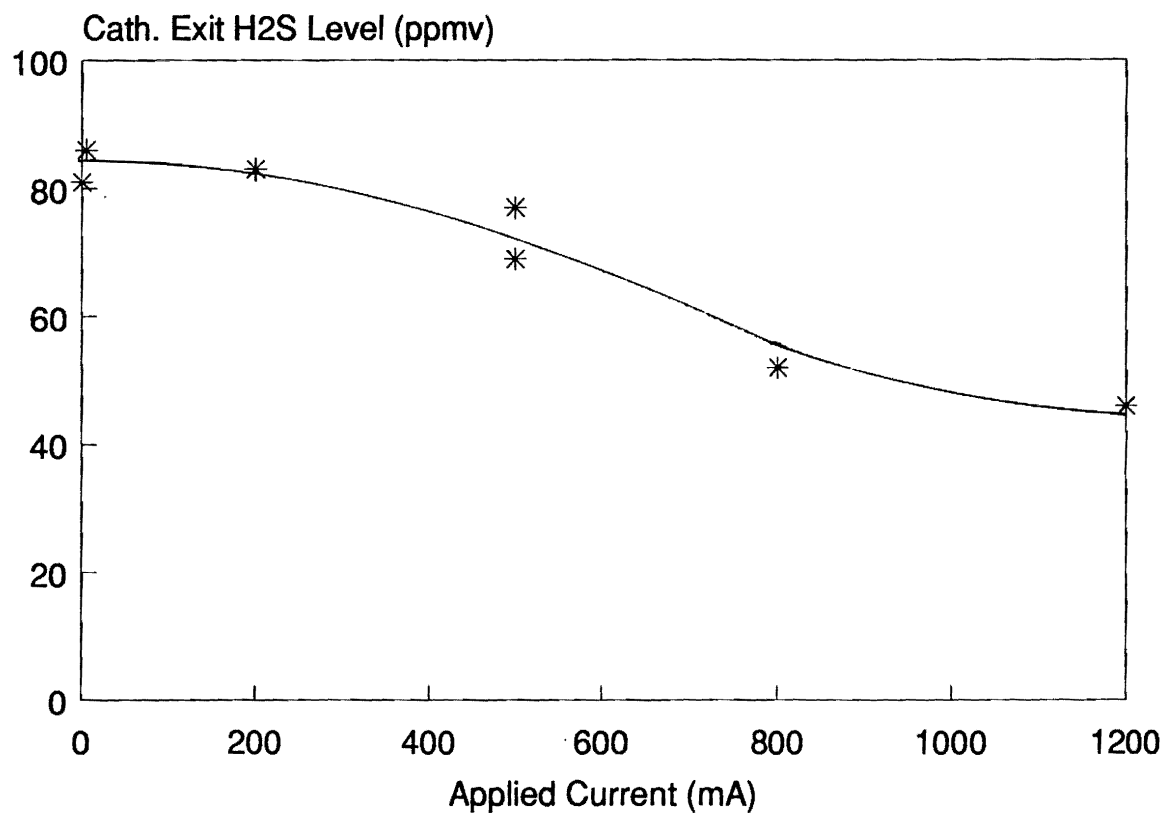
### Run 57

Both electrodes in this experiment were lithiated Ni. The membrane was two tapes of MgO with two mats of zirconia cloth. One of the zirconia mats was cut with a wick extending out of the cell and resting in an electrolyte reservoir. This was to provide a continuous supply of electrolyte to the membrane in the event of electrolyte evaporation/reaction with the cell materials. The electrolyte loaded into the cell was 0.8 mole% sulfide in a carbonate supporting electrolyte. Eutectic carbonate electrolyte was loaded into the reservoir. The cell housings were 316 stainless steel painted with aluminum.

After binder burn-out and the cell had reached run temperature, fuel gas of final composition 14.4%CO<sub>2</sub>, 45.1% CO, 6.2% H<sub>2</sub>O, 34.2% H<sub>2</sub>, and 113 ppmv H<sub>2</sub>S was fed to the cell. This gives an equilibrium sulfide level in the electrolyte of 0.63 mole% sulfide. The gas phase limiting current density under these conditions was estimated to be 1.28 mA/cm<sup>2</sup> and the membrane limiting current density was estimated at 1.97 mA/cm<sup>2</sup>.

H<sub>2</sub>S removal data (presented in Figure 3). Removal of H<sub>2</sub>S below 2 ppmv (GC detector limit) was recorded with only 5 mA (0.63 mA/cm<sup>2</sup>) applied to the cell and a cross cell potential of only -275 mV (cathode to anode). Upon shutting off applied

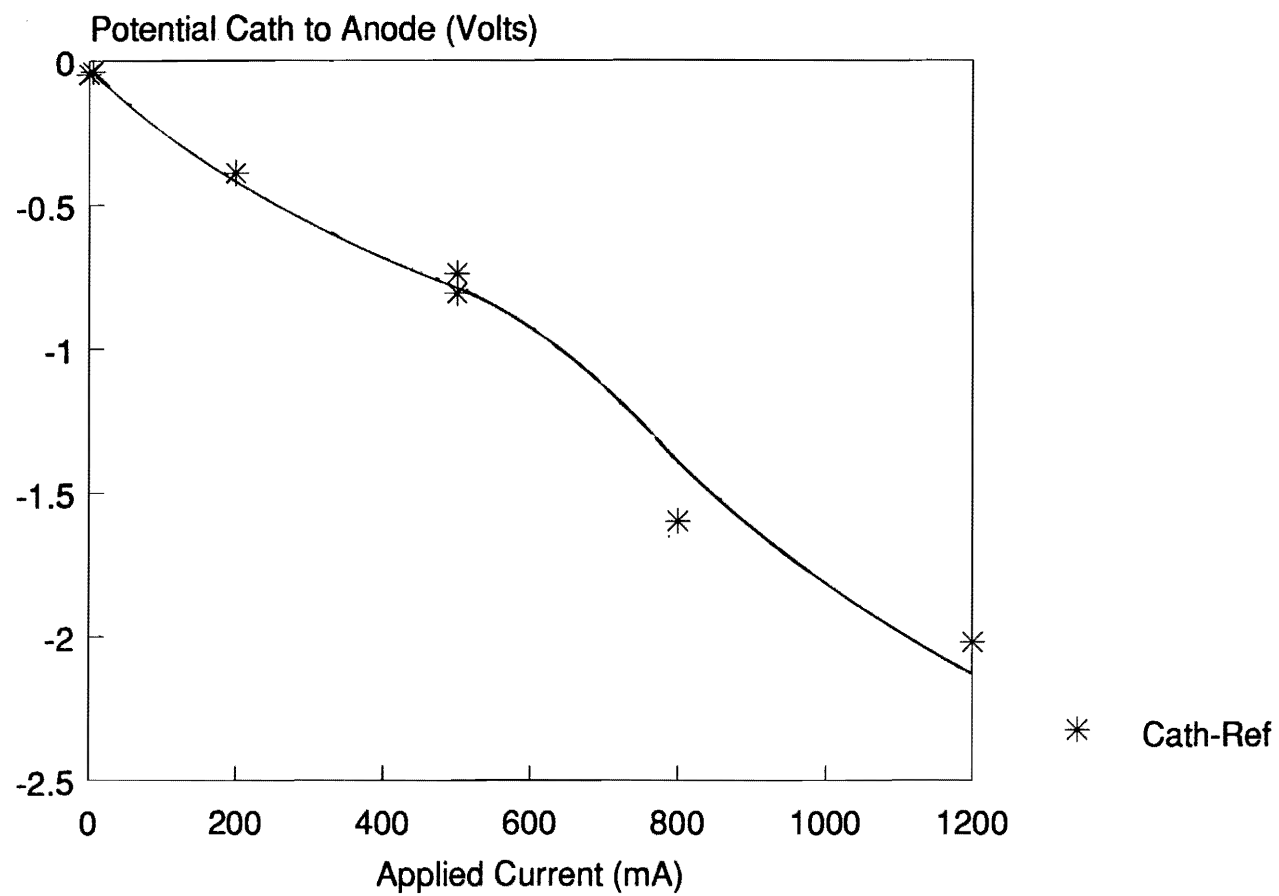
### Exit H<sub>2</sub>S Level vs Applied Current Run 56



Inlet H<sub>2</sub>S = 96 ppmv  
Cathode Flow = 235 cc/min  
Temp = 700 C

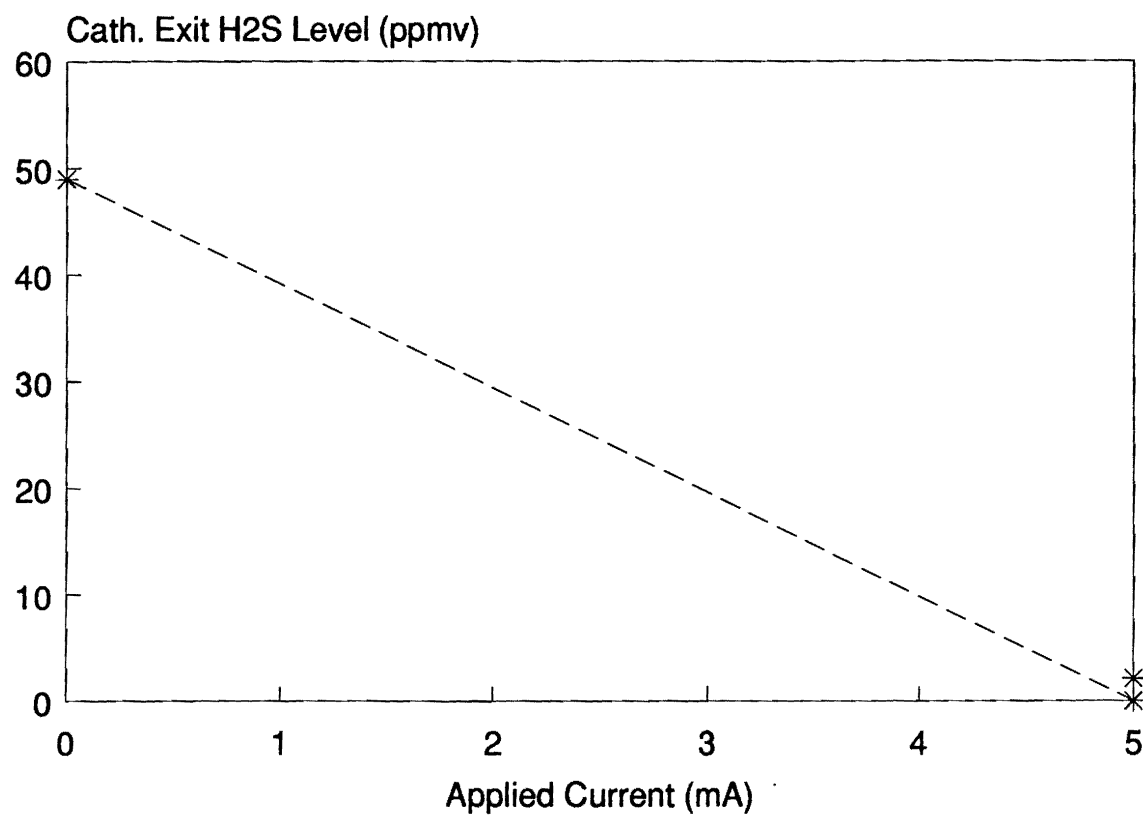
**Figure 1**

### Cross-Cell Potential vs Applied Current Run 56



**Figure 2**

# Exit H2S Level vs Applied Current Run 57



Inlet H2S = 110 ppmv  
Cathode Flow = 230 cc/min  
Temp = 700 C

**Figure 3**

current, exit  $\text{H}_2\text{S}$  levels only returned to 24 ppm (113 ppm entering the cell). The electrolyte reservoir was removed since it was a potential carbonate sink for reaction with  $\text{H}_2\text{S}$  in the gas. Cell cross flow started soon after this and the cell was shut down. Apparently, electrolyte was wicked out of the membrane onto the surface of the steel housings thereby depleting the membrane of electrolyte and allowing gas cross-over.

### Run 58

This experimental run also used lithiated Ni electrodes. In this experiment, the membrane was a hot pressed Molten Carbonate Fuel Cell (MCFC) membrane provided by Gas Research Institute (GRI). This structure is a 50/50 weight mixture of  $\text{LiAlO}_2$  and eutectic Li/K carbonate. The housings were MACOR (with a stainless steel coil in the feed gas line to act as a shift reactor) and aluminum foil gaskets were used. Excess  $\text{Li}_2\text{CO}_3$  (for reaction with the Al gaskets in conversion to  $\text{LiAlO}_2$ ) was sprinkled on the membrane surface with enough  $\text{Li}_2\text{S}$  to bring the electrolyte to 0.8 mole% sulfide.

After the electrolyte was molten, fuel gas with composition 17.3%  $\text{CO}_2$ , 42.2%  $\text{CO}$ , 3.3%  $\text{H}_2\text{O}$ , 37.1%  $\text{H}_2$ , (after shift reaction) and 117 ppmv  $\text{H}_2\text{S}$  was fed to the cell. This gives an equilibrium sulfide level of 0.65 mole%. The calculated gas phase limiting current density at this temperature was found to be  $1.31 \text{ mA/cm}^2$  and the membrane limiting current density was estimated to be  $1.53 \text{ mA/cm}^2$ .



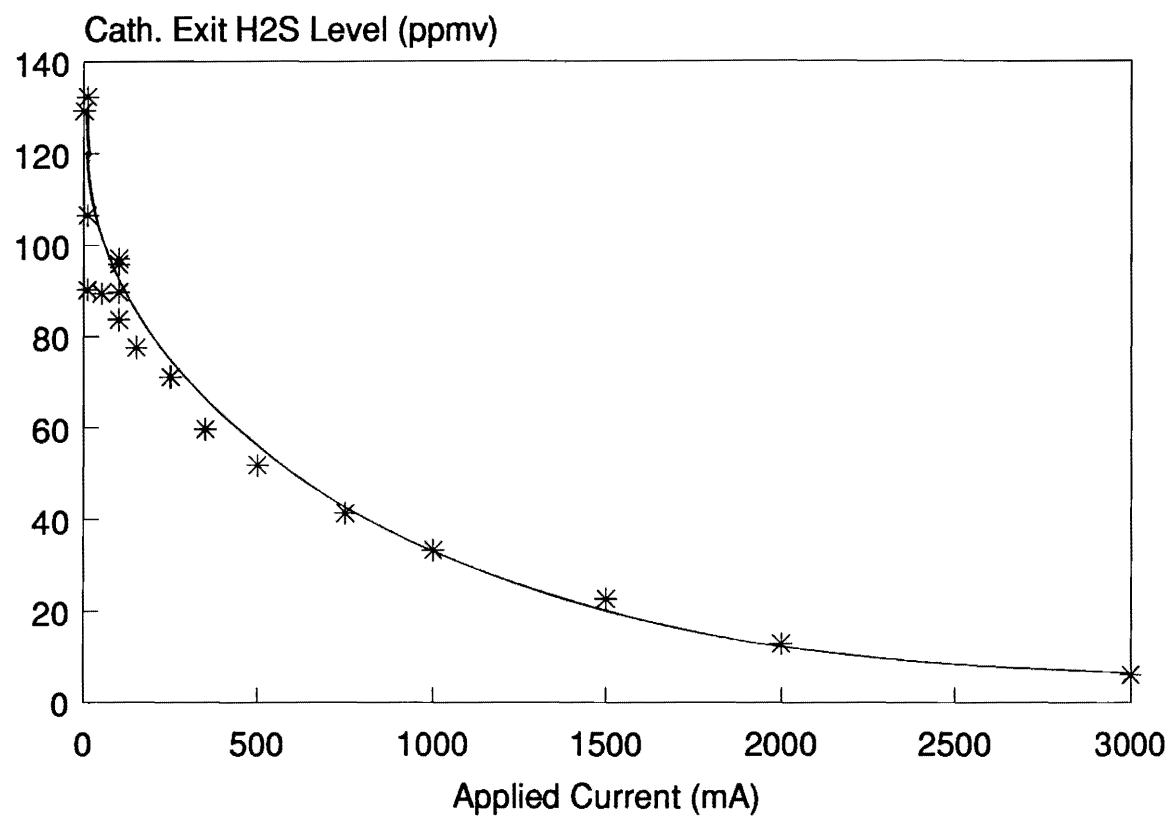
H<sub>2</sub>S removal data (see Figure 4), anodic CO<sub>2</sub> production data (see Figure 5), and cross-cell potential data (see Figure 6) was taken. Examination of Figure 4 shows the most dramatic H<sub>2</sub>S reduction takes place at currents less than 10 mA (1.23 mA/cm<sup>2</sup>). Beyond this, diffusion of H<sub>2</sub> across the cell decreases H<sub>2</sub>S current efficiencies in favor of CO<sub>2</sub> production with applied current. Cross-cell potentials were very high at large applied currents (> 500 mA). This was due to concentration effects as the cathode gas was depleted of H<sub>2</sub>O by the carbonate transport reaction. H<sub>2</sub>S levels were driven as low as 6 ppmv even with H<sub>2</sub> cross-over.

#### Run 59

This experimental run used two mats of zirconia cloth that were densified from 83% voids to 72% voids by soaking in an ethyl alcohol slurry of LiAlO<sub>2</sub> (slurry 20 wt% LiAlO<sub>2</sub>). Particles of LiAlO<sub>2</sub> were suspended within the ZrO<sub>2</sub> mesh after the water was evaporated away. No tapes of MgO were used in this experiment. The electrodes were both lithiated nickel. The electrolyte was pressed and loaded as a disk into the cell prior to heat-up. The electrolyte composition was 0.8 mole% sulfide and the balance was eutectic carbonate. The housings were MACOR and aluminum foil gaskets were used.

After melting the electrolyte into the matrix, fuel gas of composition 14.4% CO<sub>2</sub>, 45.1% CO, 6.2% H<sub>2</sub>O, and 34.2% H<sub>2</sub> (after shift reaction) with 85.7 ppm H<sub>2</sub>S was started to the cell. This gives an equilibrium sulfide level of 0.48 mole %. The gas phase limiting current density was estimated to be 1.06 mA/cm<sup>2</sup> and the membrane

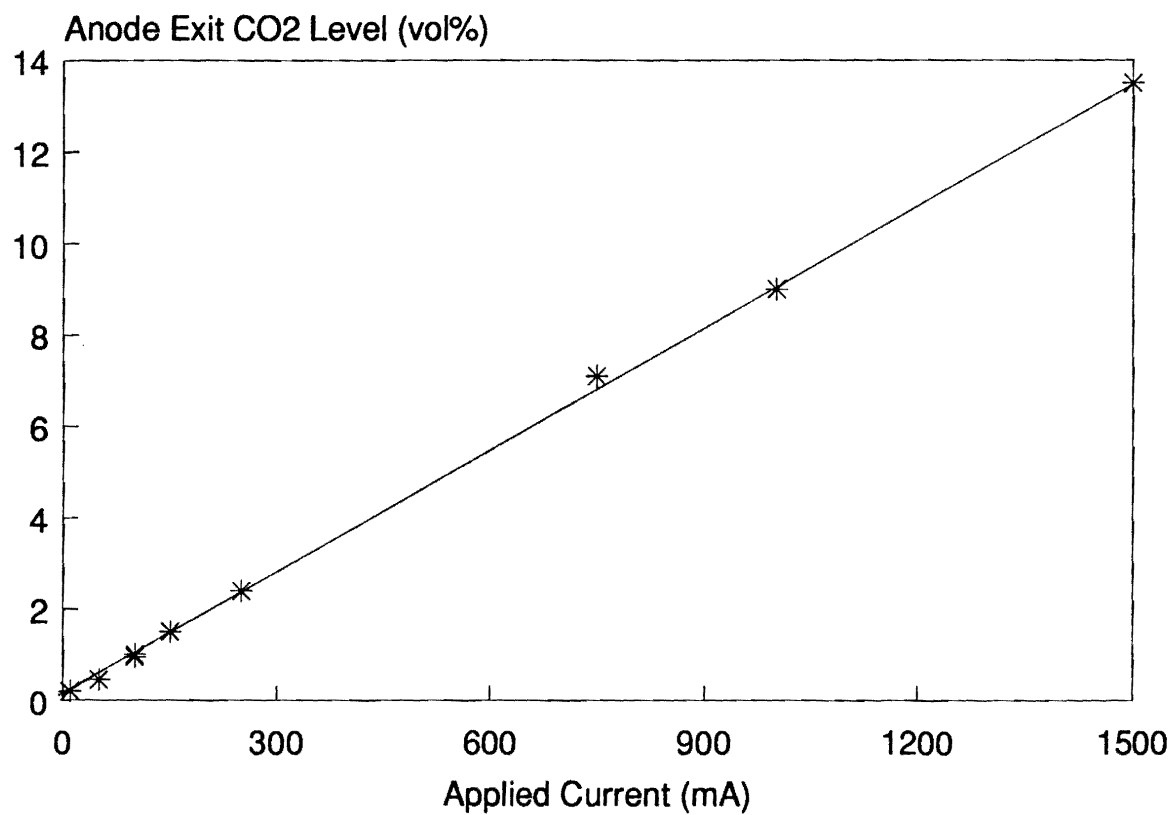
### Exit H<sub>2</sub>S Level vs Applied Current Run 58



Inlet H<sub>2</sub>S = 117 ppmv  
Cathode Flow = 200 cc/min  
Temp = 700 C

**Figure 4**

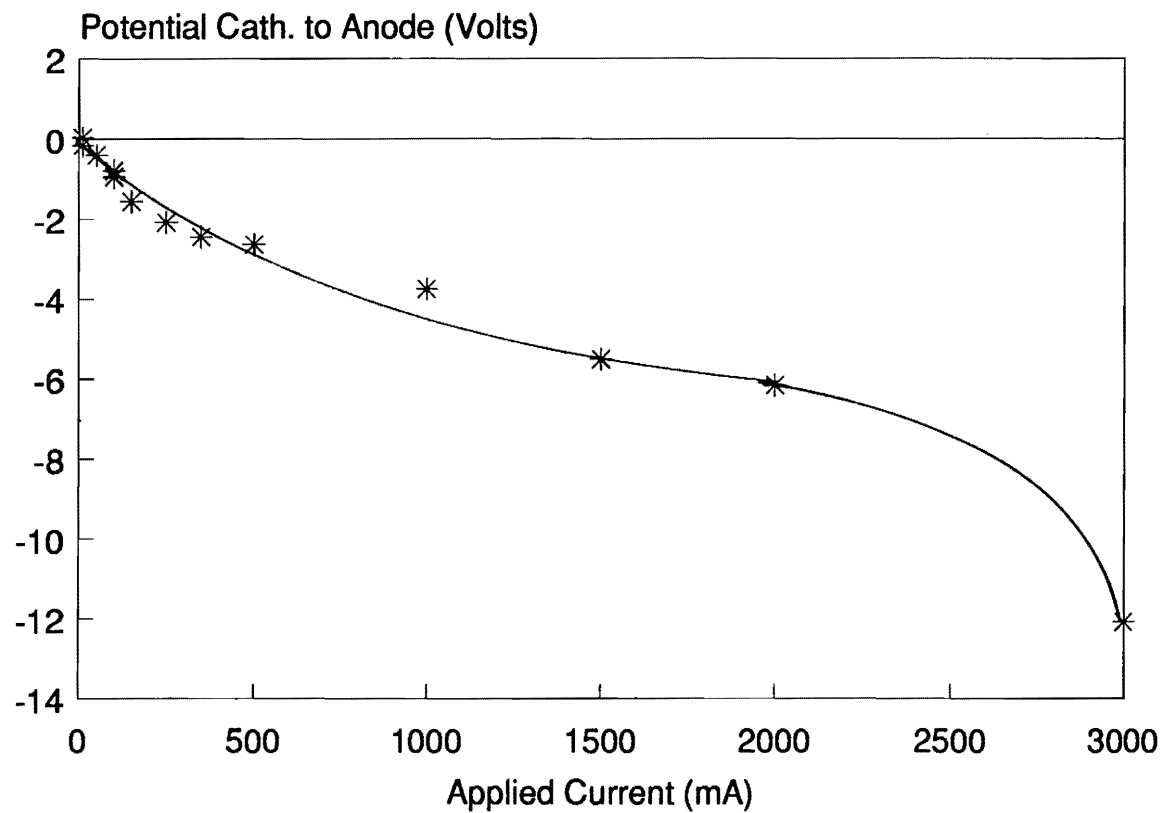
### Exit Anode CO2 Level vs Applied Current Run 58



Inlet CO2 = 0 vol%  
Anode Flow = 175 cc/min  
Temp 700 C

**Figure 5**

### Cross-Cell Potential vs Applied Current Run 58



Cathode Flow = 200 cc/min  
Anode Flow = 175 cc/min  
Temp = 700 C

**Figure 6**

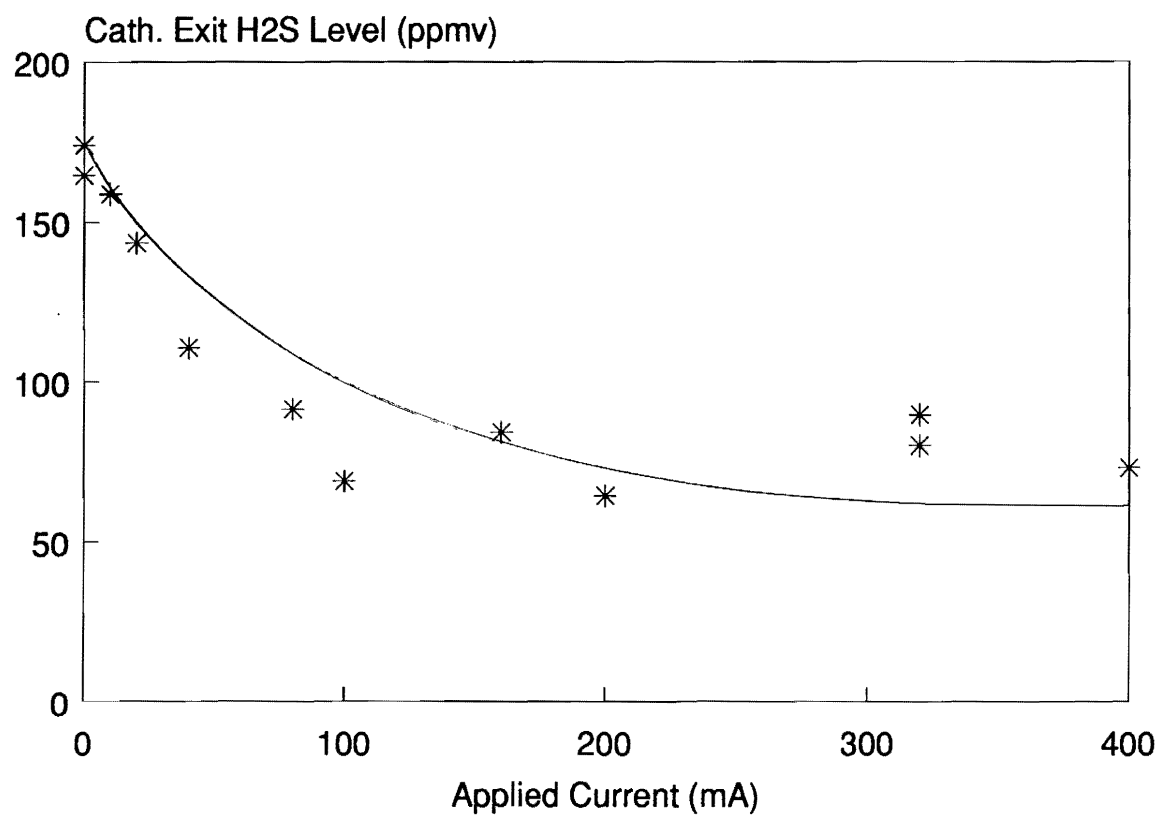
limiting current density was estimated to be  $1.5 \text{ mA/cm}^2$ .

$\text{H}_2\text{S}$  removal data (see Figure 7) and cross-cell potential data (see Figure 8) were taken. The inlet  $\text{H}_2\text{S}$  level was 85.7 ppm, but with zero current applied to the cell, the exit  $\text{H}_2\text{S}$  level was seen to be 165 ppm. This was due to excess sulfide initially present in the electrolyte. With application of current,  $\text{H}_2\text{S}$  levels were driven as low as 73 ppm with 400 mA applied to the cell ( $50.5 \text{ mA/cm}^2$ ). Hydrogen cross over hampered  $\text{H}_2\text{S}$  removal efficiency causing higher current levels to be needed to achieve removal. With higher currents came higher cross-cell potentials until the carbonate transport region was reached. Here,  $\text{H}_2\text{S}$  removal stopped due to the concentration preference for carbonate transport.

### Run 60

This experimental run used two zirconia mats that were densified with sub-micron particles of  $\text{ZrO}_2$  in aqueous solution purchased from Zircar, Inc. This rigidizer is composed of 44 wt%  $\text{ZrO}_2$ , 8 wt% Acetic acid, 3 wt%  $\text{Y}_2\text{O}_3$ , in an aqueous slurry. Mats were densified by soaking in rigidizing solution under a vacuum to pull air out of the woven cloth and facilitate complete wetting. These were then dried and soaked again. This process was repeated for three consecutive soakings. These mats were densified to 66 void%. The electrolyte was 0.8% sulfide and was pressed into a disk and loaded into the cell to be melted in-situ. The electrodes were lithiated nickel and the housings were MACOR with aluminum foil gaskets.

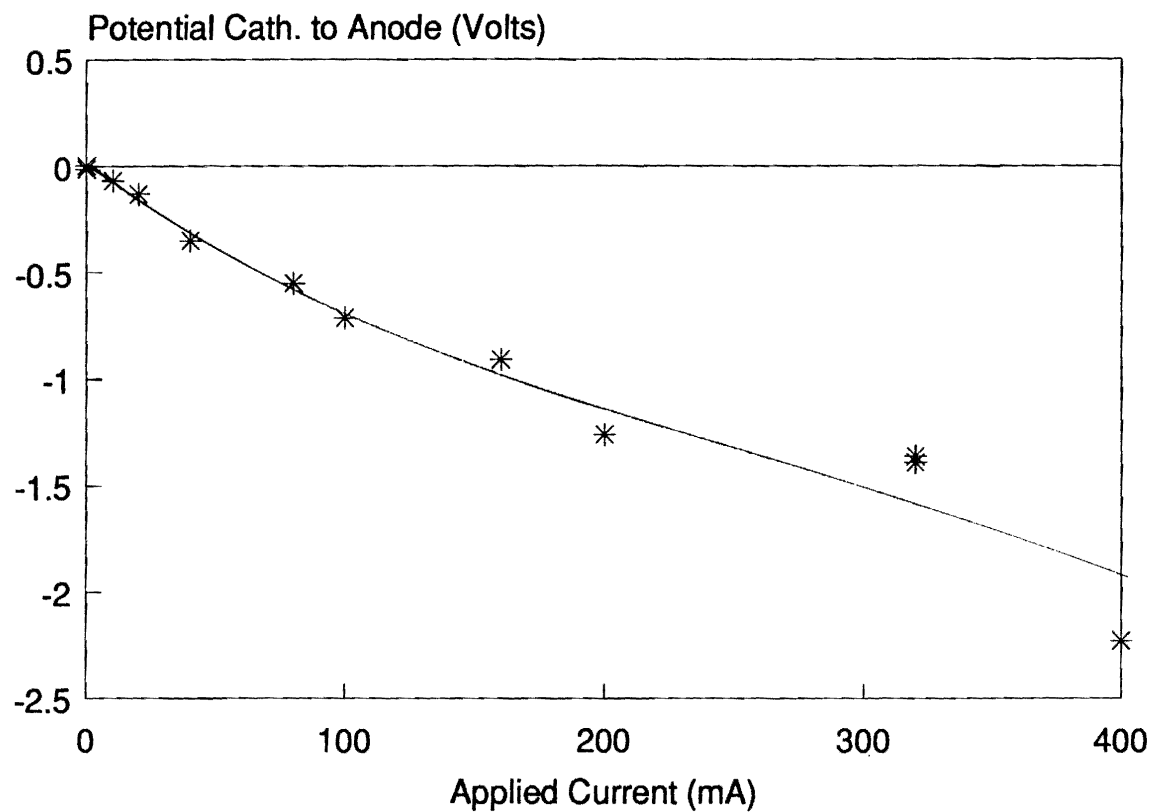
### Exit H<sub>2</sub>S Level vs Applied Current Run 59



Inlet H<sub>2</sub>S Level = 85.7 ppmv  
Cathode Flow = 237 cc/min  
Temp = 700 C

**Figure 7**

# Cross-Cell Potential vs Applied Current Run 59



Cathode Flow = 237 cc/min  
Anode Flow = 100 cc/min  
Temp = 700 C

**Figure 8**

Poor electrical contacts between the electrodes and the membrane lead to high cell resistance and high cross-cell potentials. The cell was shut down before any useful data was taken.

#### Run 61

This experimental run was identical in set up to run 60. Excess electrolyte was also added to accommodate reaction of  $\text{Li}_2\text{CO}_3$  with the Al foil to form  $\text{LiAlO}_2$ . The rate of this reaction is evidently slow, however, since the excess electrolyte flooded the anode channels and froze in the exit anode tube. This caused a pressure spike on the anode side of the cell which ruptured the membrane. The cell was shut down before any useful data was taken.

#### Run 62

This experimental run was also identical in set-up to run 60. The zirconia mats were densified to 64 void %. Only enough electrolyte was added to wet the membrane, extra electrolyte was slowly added after the cell had reached run temperature to react with the Al gaskets.

Once the electrolyte had melted, fuel gas of composition 14.4%  $\text{CO}_2$ , 45.1%  $\text{CO}$ , 6.2%  $\text{H}_2\text{O}$ , 34.2%  $\text{H}_2$  (after the shift reaction at  $700^\circ\text{C}$ ) with 120.4 ppmv  $\text{H}_2\text{S}$ .  $\text{H}_2\text{S}$  removal data was taken at 216 cc/min and a temperature of  $700^\circ\text{C}$ . At this temperature and gas composition, the equilibrium sulfide level in the electrolyte is calculated to be 0.68%. The gas phase limiting current density is  $1.33 \text{ mA/cm}^2$  and



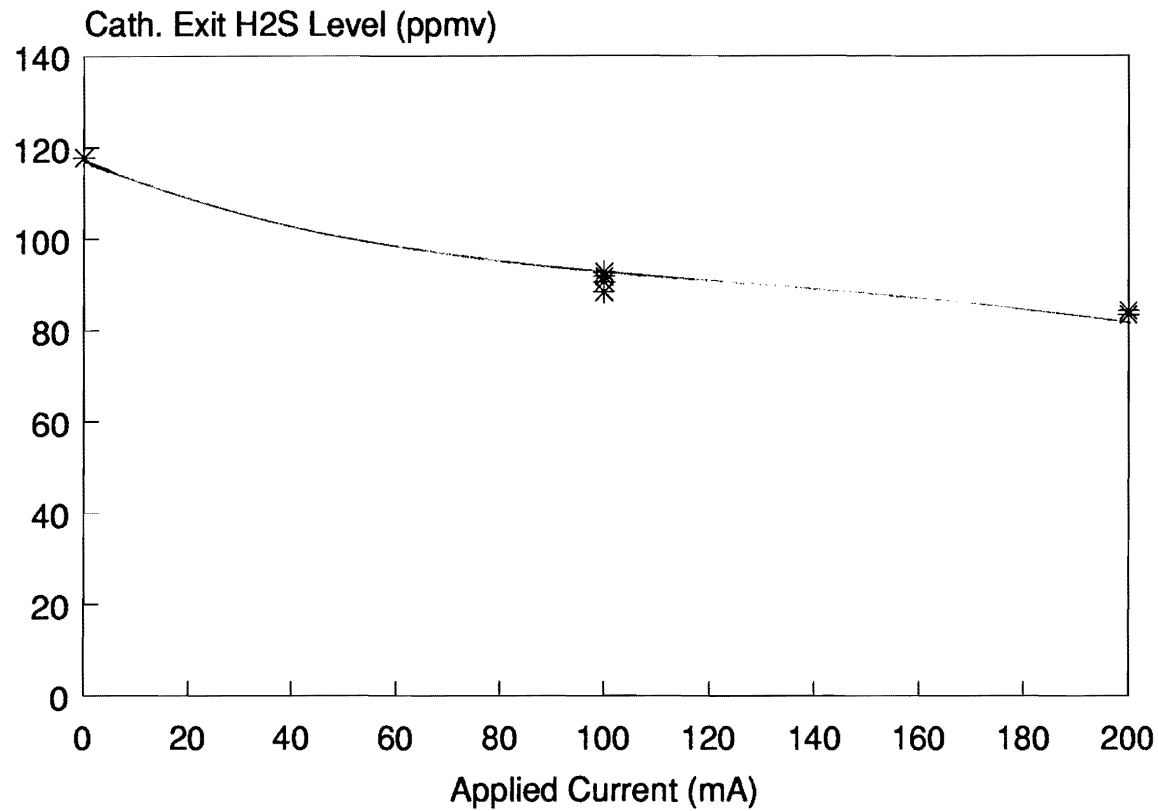
the membrane limiting current density is  $2.10 \text{ mA/cm}^2$ . A second set of  $\text{H}_2\text{S}$  removal data was taken at a flow of  $100 \text{ cc/min}$  and a temperature of  $750^\circ\text{C}$  (gas composition  $13.6\% \text{ CO}_2$ ,  $45.8\% \text{ CO}$ ,  $6.9\% \text{ H}_2\text{O}$ ,  $33.4\% \text{ H}_2$  with  $93.6 \text{ ppmv H}_2\text{S}$ ) (see Figures 9 and 10). At this temperature and gas composition, the membrane equilibrium sulfide level was estimated to be  $0.91 \text{ mole\% sulfide}$ . The gas phase limiting current density was estimated to be  $1.15 \text{ mA/cm}^2$  and the membrane limiting current density  $2.82 \text{ mA/cm}^2$ . Anodic  $\text{CO}_2$  production was also monitored (see Figures 11 and 12) and cross-cell potentials were recorded for  $100 \text{ cc/min}$  and run temperature of  $750^\circ\text{C}$  (see Figures 13). Comparison of Figures 9 and 10 shows that  $\text{H}_2\text{S}$  removal efficiency is improved by lower flow rates (higher residence time) and higher temperatures (higher limiting current densities).

### Run 63

This experimental run used  $\text{Si}_3\text{N}_4$  tapes with vinyl binder as the membrane support material. Eutectic carbonate electrolyte was also added to the membrane by mixing in a 50/50 weight mixture with the same binder material and laminating the structure together under pressure. The electrodes in this experiment were both lithiated Ni and the housing was MACOR. No aluminum foil gaskets were used.

The cell was heated under  $\text{O}_2$  to  $520^\circ\text{C}$ . Cross-flow between the cathode and the anode side of the cell indicated that the membrane had lost integrity. No amount of electrolyte added corrected the situation. The cell was shut down before any useful

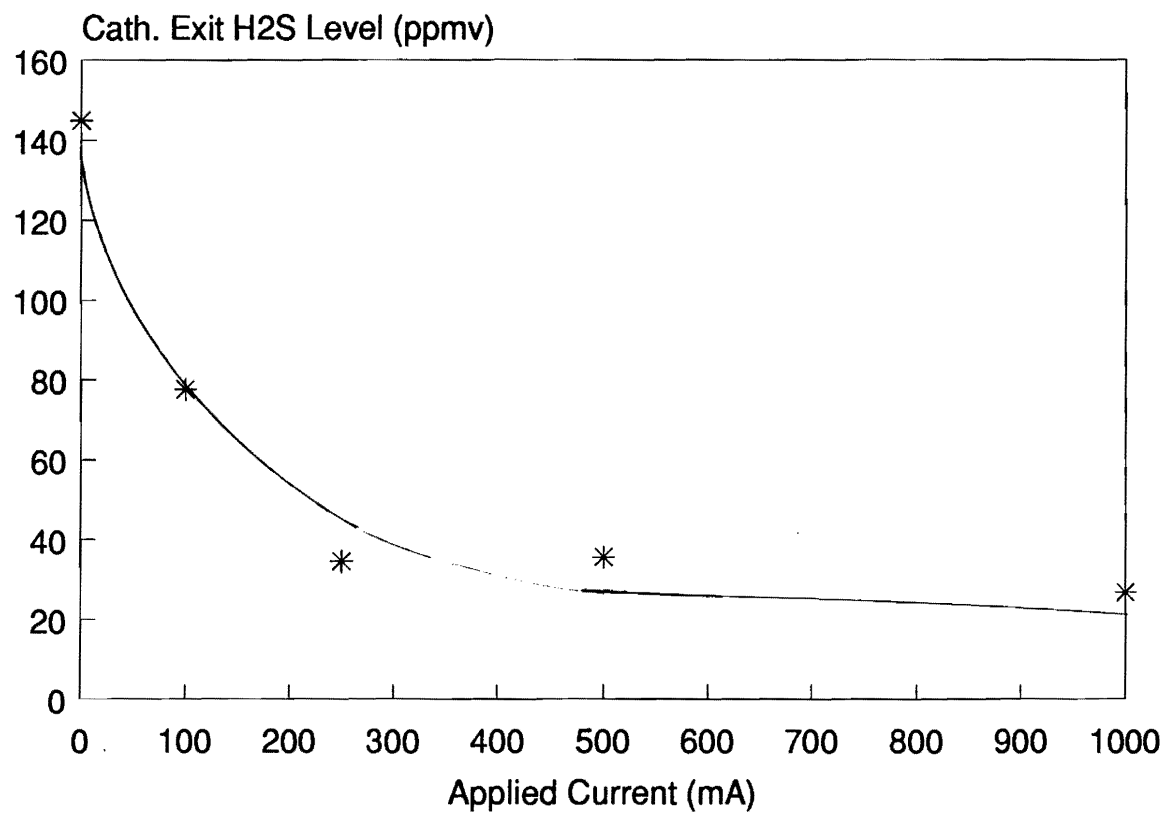
### Exit H<sub>2</sub>S Level vs Applied Current Run 62



Inlet H<sub>2</sub>S Level = 120.4 ppmv  
Cathode Flow = 216 cc/min  
Anode Flow = 42 cc/min

**Figure 9**

### Exit H<sub>2</sub>S Level vs Applied Current Run 62



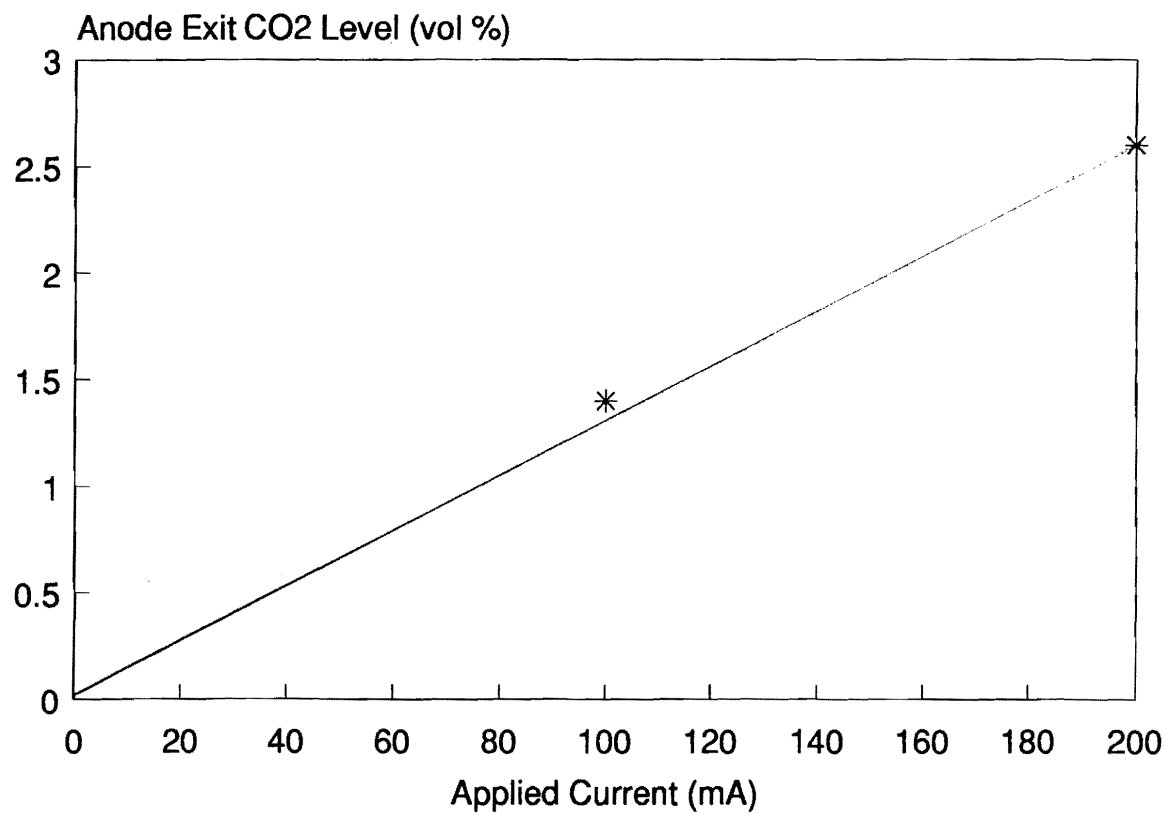
Inlet H<sub>2</sub>S Level = 93.6 ppmv

Cathode Flow = 100 cc/min

Temp = 750 C

**Figure 10**

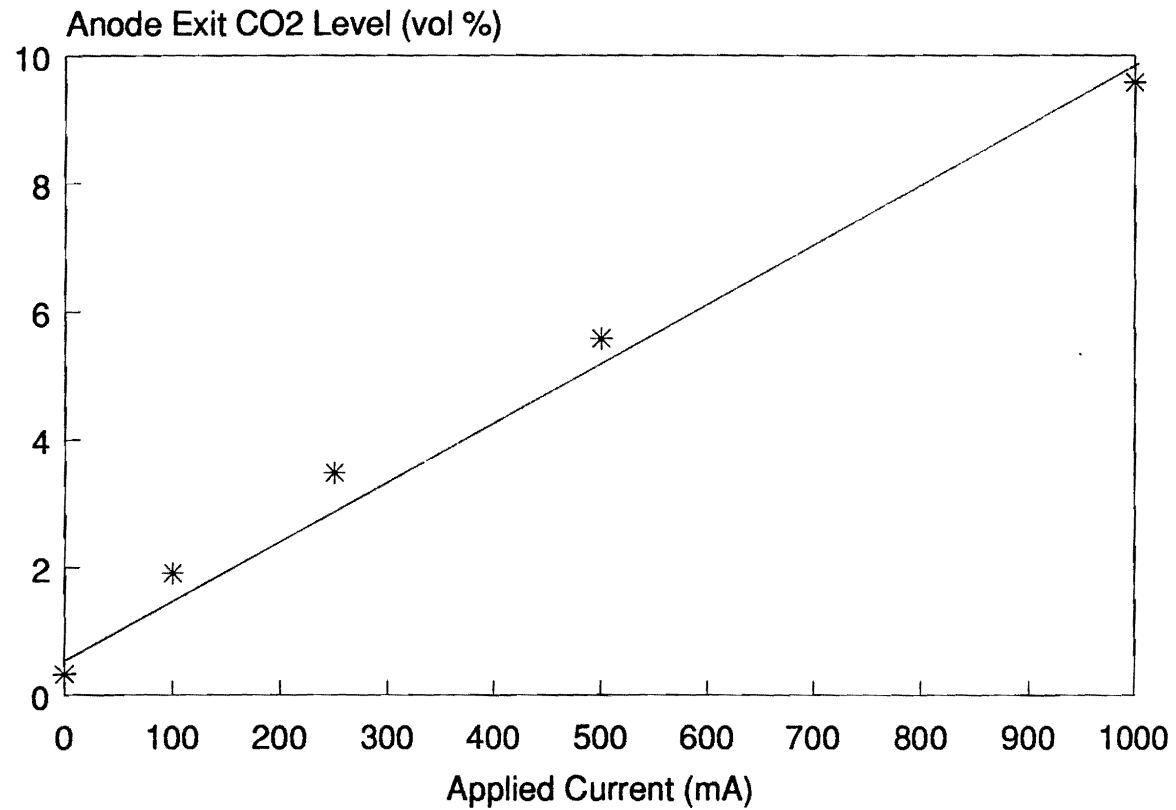
### Exit Anode CO<sub>2</sub> Level vs Applied Current Run 62



Inlet CO<sub>2</sub> Level = 0%  
Anode Flow = 42 cc/min  
Temp = 700 C

**Figure 11**

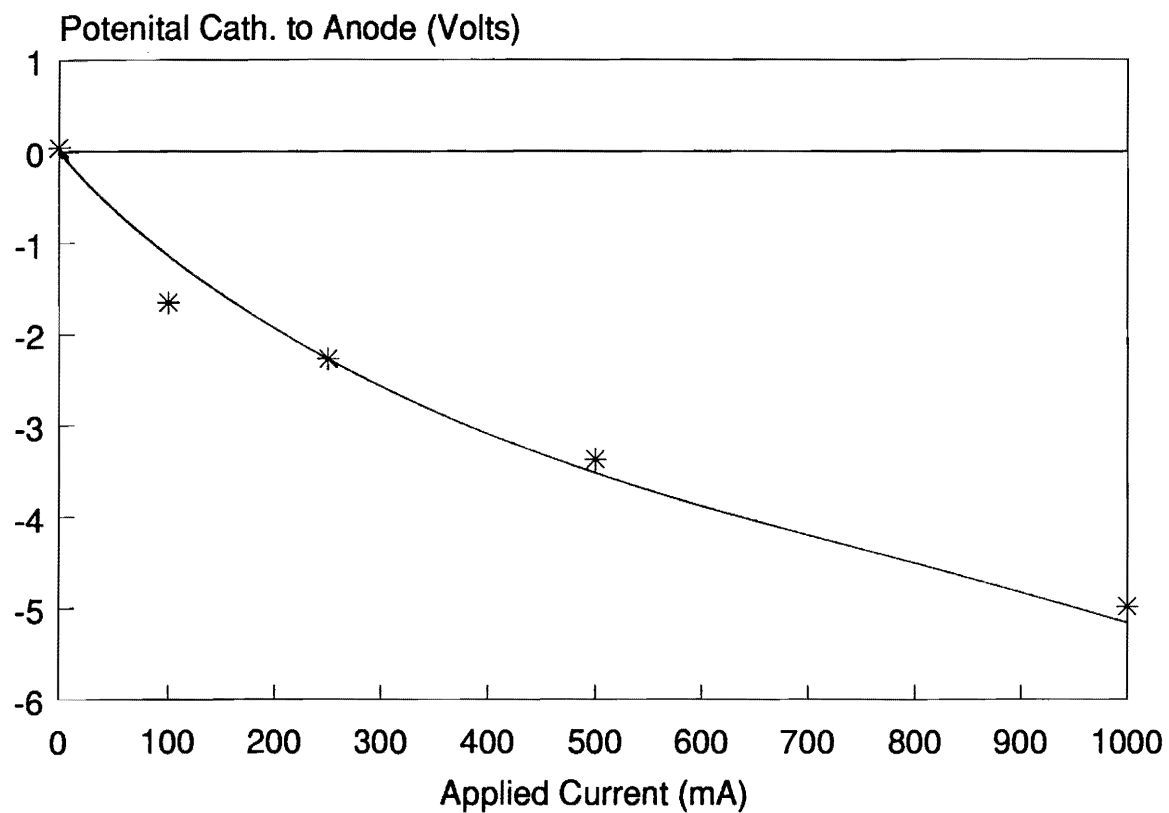
### Exit Anode CO2 Level vs Applied Current Run 62



Inlet CO2 Level = 0%  
Anode Flow = 58 cc/min  
Temp = 750 C

**Figure 12**

### Cross-Cell Potential vs Applied Current Run 62



Cathode Flow = 100 cc/min  
Anode Flow = 58 cc/min  
Temp = 750 C

**Figure 13**

data could be taken.

#### Run 64

This experimental used lithiated Ni as both the cathode and the anode. The membrane was a single mat of 15 mil thick zirconia cloth which was rigidized to 66 void%. This was layered with two tapes of MgO within the vinyl binder. The housings were MACOR and no gaskets were used. The electrolyte was soaked into the electrodes previous to run start-up. Since the electrodes could not hold all of the required electrolyte, the remainder was sprinkled onto the membrane before assembly.

The cell was heated under O<sub>2</sub> to 300°C over a 3 hour period and then switched to N<sub>2</sub> for the final heating to 600°C. No seals were formed on either side of the cell. Cross-flow between the cathode and the anode could not be controlled. When the cell was shut down, it was seen that carbon build-ups had formed the cell housings apart and damaged the membrane. This was from pyrolyzed binder material from incomplete burn-out. No useful data was taken.

#### Run 65

This experimental run used 1 mat of 30 mil zirconia cloth which was rigidized to 60.8% and two tapes of MgO/ZrO<sub>2</sub> in vinyl binder. The electrolyte was eutectic carbonate and was added to the cell as a pressed disk. the electrodes were lithiated

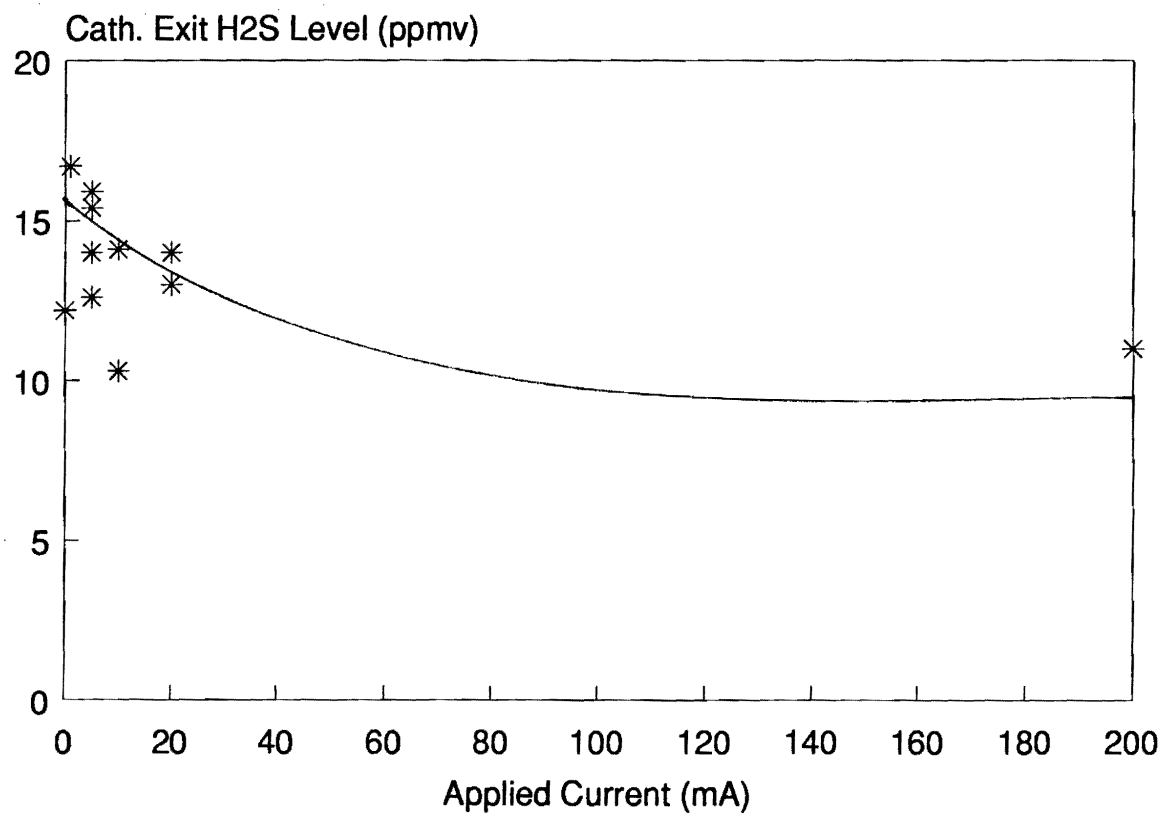
Ni. The housings were MACOR and Al foil gaskets were used. The run temperature was 650°C.

After binder burnout and electrolyte melting, fuel gas of composition 15.2% CO<sub>2</sub>, 44.2% CO, 5.4% H<sub>2</sub>O, 35.0% H<sub>2</sub> with 18.8 ppmv H<sub>2</sub>S was put through the cell. This gas composition and temperature gives an equilibrium membrane sulfide level of 0.06 mole% sulfide. The gas phase limiting current density is estimated to be 0.18 mA/cm<sup>2</sup> and the membrane limiting current density is 0.34 mA/cm<sup>2</sup>.

H<sub>2</sub>S removal data was taken at cathodic flow rates of 200 cc/min and 100 cc/min (see Figures 14 and 15). Cell polarization data was also take at these flow rates (see Figures 16 and 17). Anodic CO<sub>2</sub> production data was also taken at cathodic flow of 100 cc/min (see Figure 18).



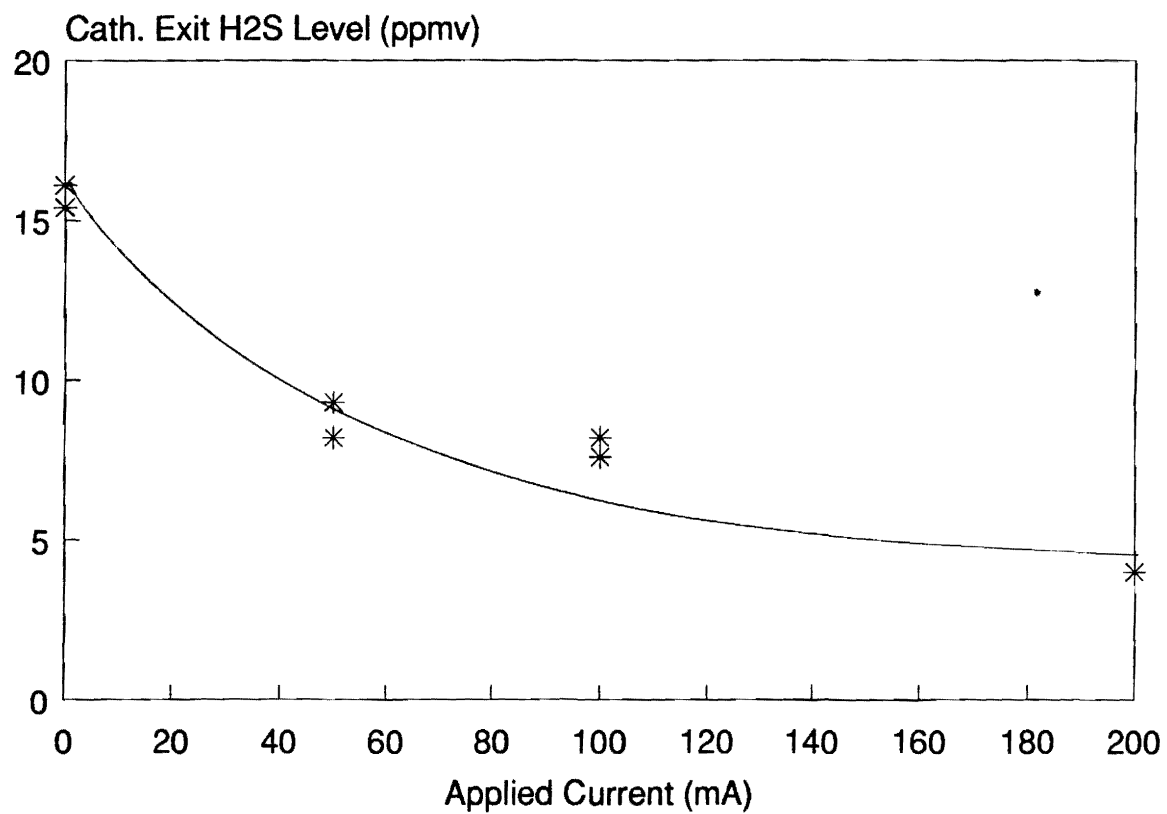
### Exit H<sub>2</sub>S Level vs Applied Current Run 65



Inlet H<sub>2</sub>S Level = 18.8 ppmv  
Cathode Flow = 200 cc/min  
Temp = 650 C

**Figure 14**

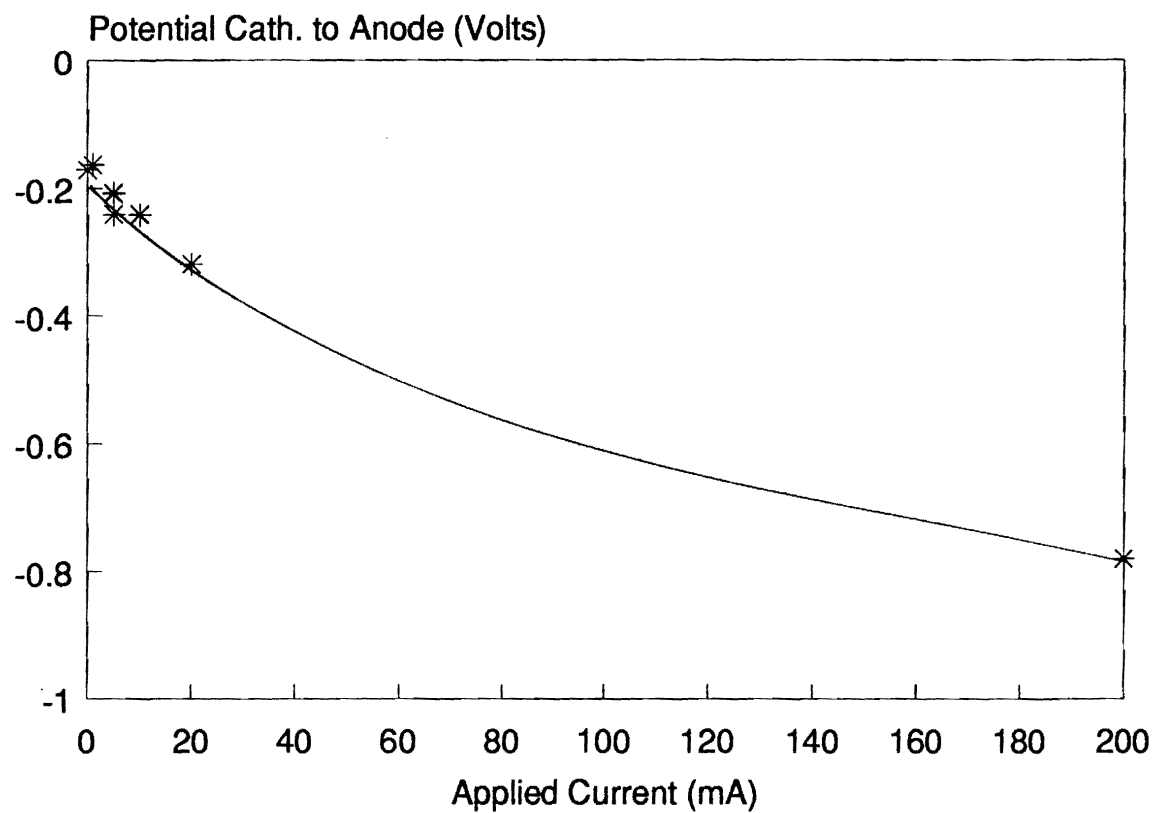
### Exit H<sub>2</sub>S Level vs Applied Current Run 65



Inlet H<sub>2</sub>S = 27 ppmv  
Cathode Flow = 100 cc/min  
Temp = 650 C

**Figure 15**

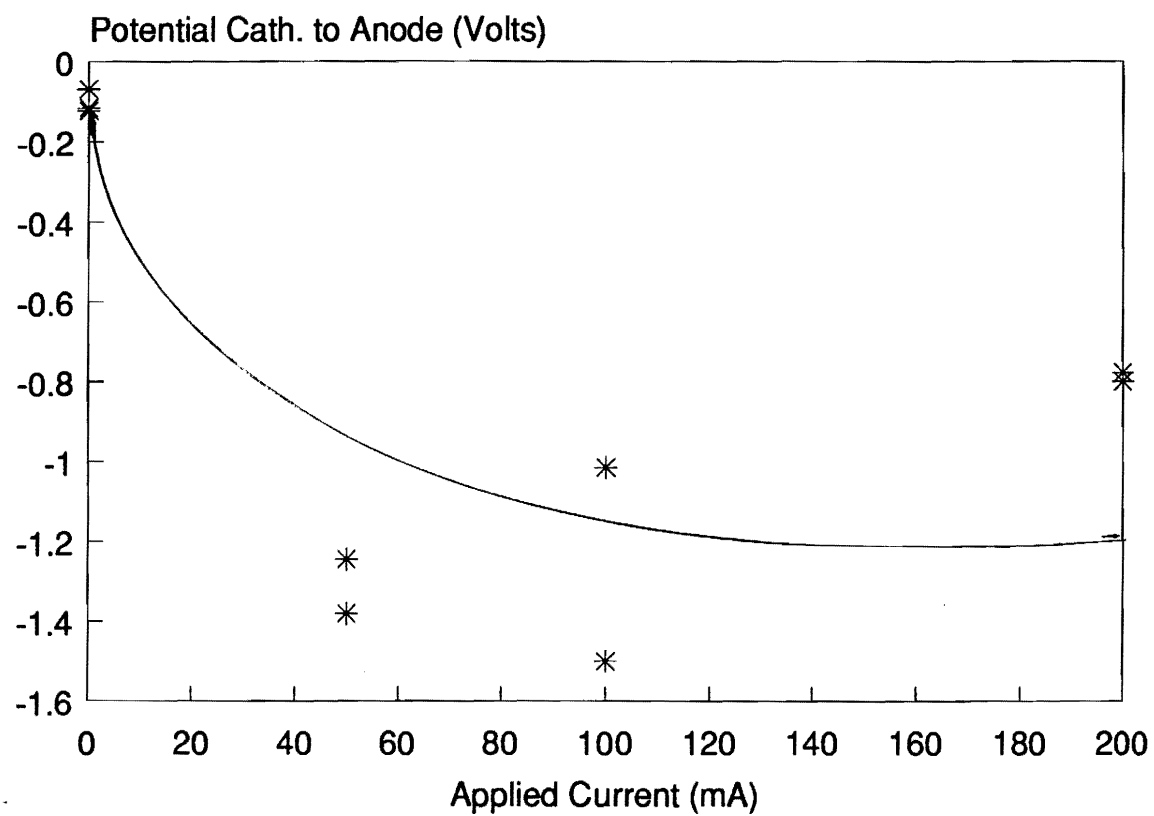
### Cross-Cell Potential vs Applied Current Run 65



Cathode Flow = 200 cc/min  
Anode Flow = 100 cc/min  
Temp = 650 C

**Figure 16**

# Cross-Cell Potential vs Applied Current Run 65



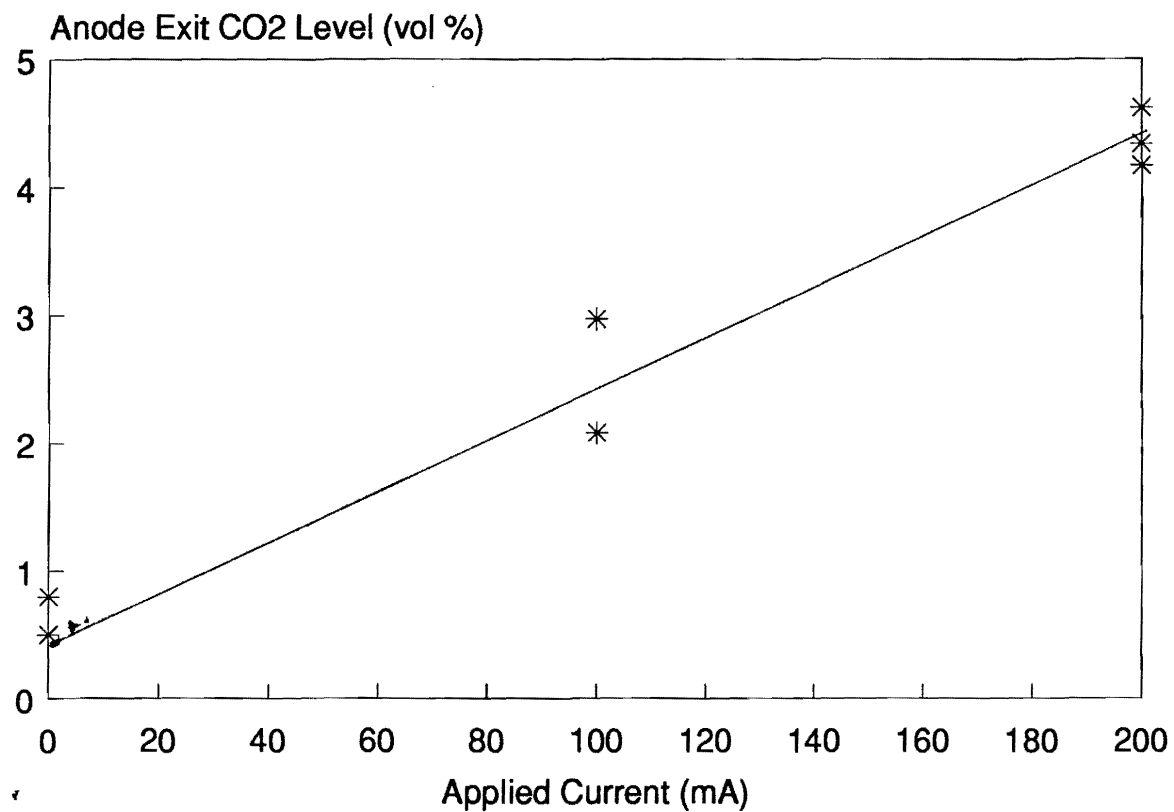
Cathode Flow = 100 cc/min

Anode Flow = 100 cc/min

Temp = 650 C

**Figure 17**

# Exit Anode CO2 Level vs Applied Current Run 65



Inlet CO2 Level = 0 %  
Anode Flow = 100 cc/min  
Temp = 650 C

**Figure 18**

**Summary**

Polishing application (100 ppmv  $\text{H}_2\text{S}$  to less than 5 ppmv  $\text{H}_2\text{S}$ ) of this technology to coal gasification synthesis gas has been repeated with both MACOR and 316 Stainless Steel housings. Polishing application has further been demonstrated at removing  $\text{H}_2\text{S}$  to below 5 ppmv with only 16 ppm entering the cell.

**Planned Work for Next Quarter**

Work will continue with the stainless steel housings. Priority will be placed on improving  $\text{H}_2\text{S}$  removal efficiency by developing even more  $\text{H}_2$  impermeable membranes.

## II. SO<sub>x</sub> Removal Cell

### Introduction

The key to the successful application of this removal method is the development of a membrane capable of achieving a current density of 50 mA/cm<sup>2</sup> at total voltages of approximately 1 Volt. Flooding of the electrode pores has been identified as a problem, leading to increased polarizations over time. To reduce flooding, new materials and fabrication methods will be investigated to produce a homogeneous, theoretically dense membrane. The matrix material must have the proper particle size distribution to develop sufficient capillary forces to prevent the electrode from flooding.

The technique used for construction of the ceramic membranes or 'tiles' is tape casting. The matrix material is mixed with an organic binder in a solvent. This mixture is poured at a constant thickness, maintained by an overhead doctor blade. The solvent is then allowed to evaporate, leaving the 'green' tape. This flexible tape is cut to the desired shape and pre-burned: placed in an oven at relatively low temperatures (<170° C), the tape is heated to remove a large amount of the solvent that is present before it is placed into a cell. The organic material is burned off in an oxygen atmosphere, leaving the desired rigid body of the porosity needed for the final tile. Electrolyte is then added at operating temperature. Pore size for the matrices used this quarter has been determined to be approximately 0.2µm.

The electrodes, unless otherwise stated, are Fibrex Ni sheets, commercially available, cut to a diameter of approximately 20 cm<sup>2</sup> area. Before placement into the

cell, they are oxidized to NiO, and lithiated to become a p-type semiconductor, in which conductivity increases with temperature. Resistance at room temperature has been measured at approximately  $2\ \Omega$ . Current travels from the stainless steel housings to the electrode through contact made with the housing. Pore size of the electrodes used this quarter was approximately  $1.0\ \mu\text{m}$ . The electrolyte is made of a mixture of 10wt%  $\text{V}_2\text{O}_5$  and 90wt%  $\text{K}_2\text{S}_2\text{O}_7$  in all cases. The gas mixture run over the cathode (reducing) side of the cell is composed of 0.3%  $\text{SO}_2$ , 3%  $\text{O}_2$ , and 96.7%  $\text{N}_2$ , except in noted cases, and all  $\text{SO}_2$  is oxidized by platinum pellets to  $\text{SO}_3$  prior to cell entry.

## Summary

Experiments performed this quarter were attempted with new materials and methods. Fabrication of electrolyte tapes was attempted upon the evaluation of Run 3. The seal formed with the electrolyte 'in situ' was found to be superior to past experiments. Fabrication of tapes and disks for introduction of the electrolyte to the cell 'in situ' have been explored.

The electrodes obtained from the Energy Research Corporation (E.R.C) were also used in a full scale experiment. The past problem of flooding due to the relatively small interstitial electrode pore size was addressed through the use of smaller ceramic particles in constructing the ceramic matrix. These attempts were not successful, but did reveal various properties of the components used.

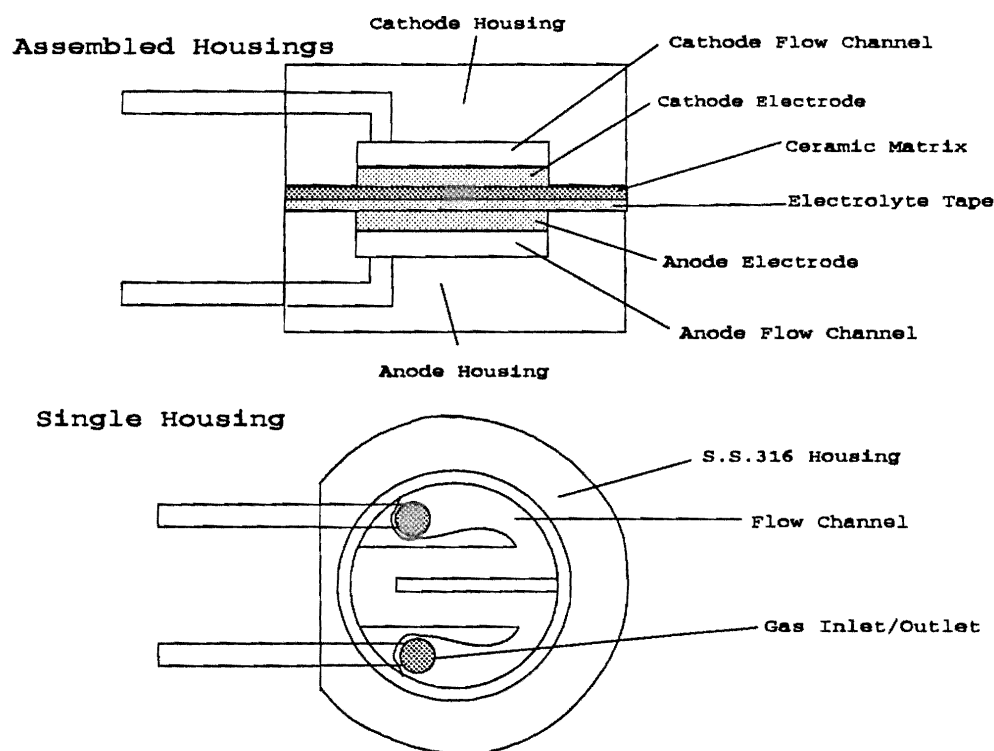
Finally, density and surface tension experiments were performed on the electrolyte. The density experiment provided an estimate of  $1.997\ \text{g/ml} \pm 0.05\ \text{g/ml}$ .



This number was then utilized in two separate attempts at determining the surface tension of the electrolyte at operating temperature. The surface tension experiments agreed within 33%.

### Full Scale Testing

The first full scale test this quarter is a continuation of the last reported



**Figure 19:** Housings used for full scale testing, with the placement of electrolyte disks noted.

test, Run 3. It was reported the inability to achieve mass balances might be due to the presence of organics from the binder volatilization in the electrolyte tape incorporated into the cell<sup>1</sup> as shown in Figure 1. Upon voluntary shutdown and

evaluation of the membrane, it was determined that the strong seal (gas crossover of 0.5 cm<sup>2</sup> every 2-5 seconds at a back pressure of 2 in. H<sub>2</sub>O) developed during the run was not due to organics. No organic material or discoloration of any part of the system was observed, indicating that the strength of the seal was due entirely to the electrolyte.

Analysis of the polarizations yielded an average exchange current density ( $i_o$ ) of 0.0792 mA/cm<sup>2</sup> for varying O<sub>2</sub> partial pressure. Exchange current densities varied inversely with O<sub>2</sub> partial pressure as seen in Table I.

**Table I: Run 3**

P(O <sub>2</sub> ) [atm]	$i_o$ [mA/cm <sup>2</sup> ]
0.12	0.0498
0.06	0.0821
0.03	0.135

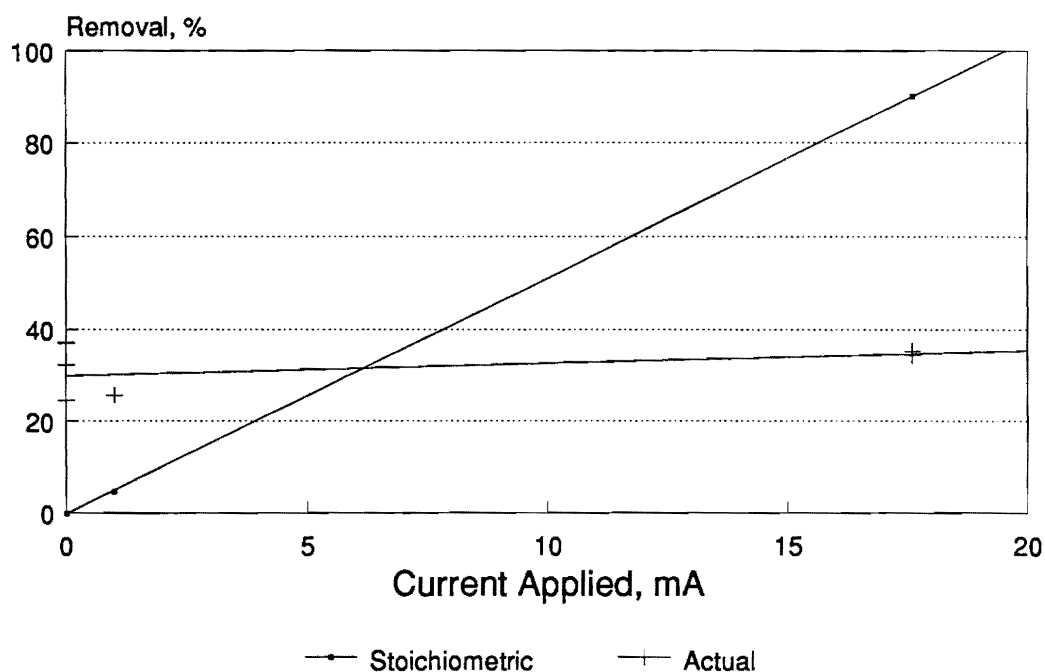
Run 4, the next full scale test, attempted to confirm the sealing ability of the electrolyte tape, with 78% of the electrolyte needed in the cell being introduced in the tape. One change made to the system was the introduction of "Liquid Steel," a commercially available product distributed by Loctite Corporation, to the cell in an attempt to ensure conductivity between the electrodes and the housing. The "Liquid Steel" had been previously tested to verify conductivity at the high cell temperatures.

Run 4 exhibited inhibiting resistances, despite conformation of the conductivity of each individual part of the cell. Attempting to resolve this crisis resulted in the rupturing of the cell and the ceramic membrane; the test was terminated. Evaluation revealed the "Liquid Steel" had not performed as expected, exhibiting a resistance of

12-20 k $\Omega$ . This could be due to the resins present, eliminating a current path. Further use of "Liquid Steel" was discontinued.

Run 5 used electrolyte 'in situ,' in the form of a hot-pressed disk consisting of 66.7 wt% electrolyte and 33.3 wt% polyethylene oxide (MW=900,000). Further details

## SO<sub>2</sub> Removal - Run 5



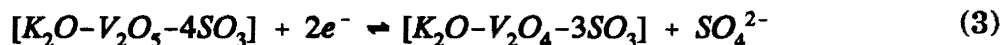
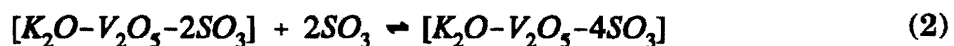
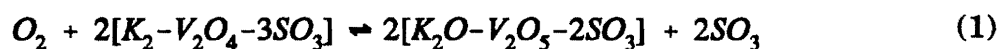
7/2/92

**Figure 20:** Removal rates for Run 5 versus stoichiometric removal at various applied currents.

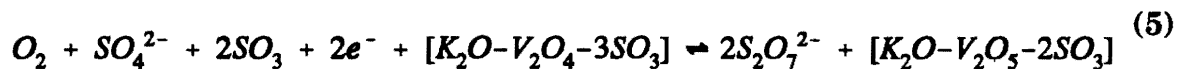
on electrolyte disk manufacture will be discussed later in this report. Heating of the cell proceeded under an oxygen atmosphere. Seals in the cell were determined to be excellent, holding 1.5-2.5 in.H<sub>2</sub>O back pressure. Cell performance, however, was unsatisfactory; apparent removal was below stoichiometric levels (see Figure 2). Cell

polarization (see Figure 3) shows a total cell potential of 0.5 V at low applied currents. As the current across the cell was increased to 150 mA, corresponding to a 61.7% stoichiometric removal level, the galvanostat overloaded. Anodic voltage was observed to reach levels as high as 15 V, with the IR drop being virtually equivalent to the voltage as shown in Figure 4. The cell was shut down due to the large anodic resistance.

One possible explanation for the low removal is the removal of  $O_2$  and  $SO_2$  to form pyrosulfate through a complex of reactions utilizing complexes of vanadium



pentoxide. The sum of the reactions contained in equations (1) through (4) is shown

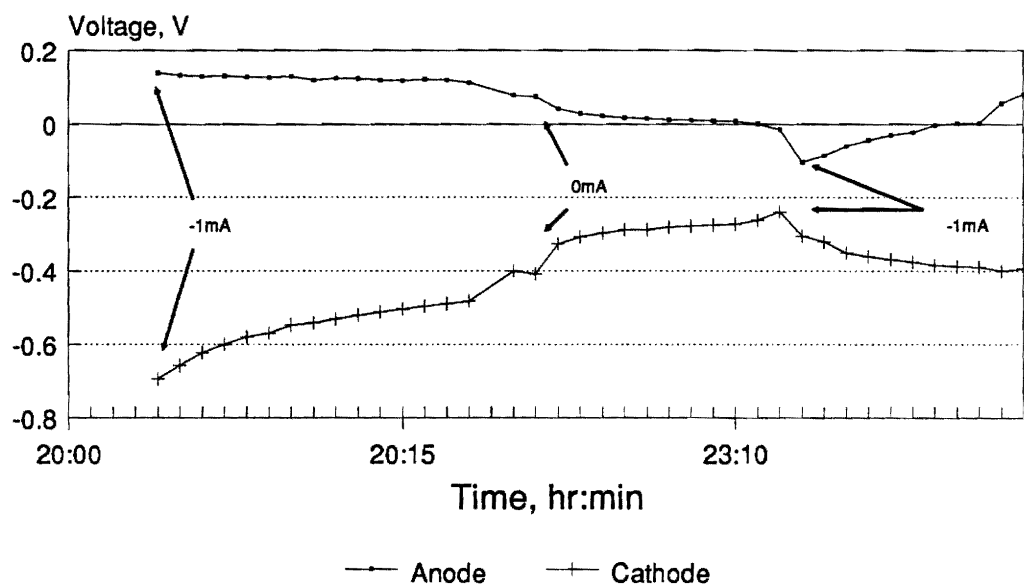


in equation (5). The net result is the formation of pyrosulfate and a vanadium oxide complex through the utilization of oxygen, sulfate, and sulfur trioxide, and the use of two electrons. This mechanism is suggested by McHenry<sup>2</sup>, and could explain the

apparent difference between the stoichiometric removal levels, and the actual removal levels.

Upon breakdown of the cell, it was noted that both the anode and cathode electrodes exhibited excellent conductivity;  $0.6\text{--}1\Omega$  at room temperature on both sides. The conductivity from the anode electrode to the anode housing, the cause of the

## Polarization Run 5



1mA, 0mA, 1mA at 50cc/min  
7/2/92

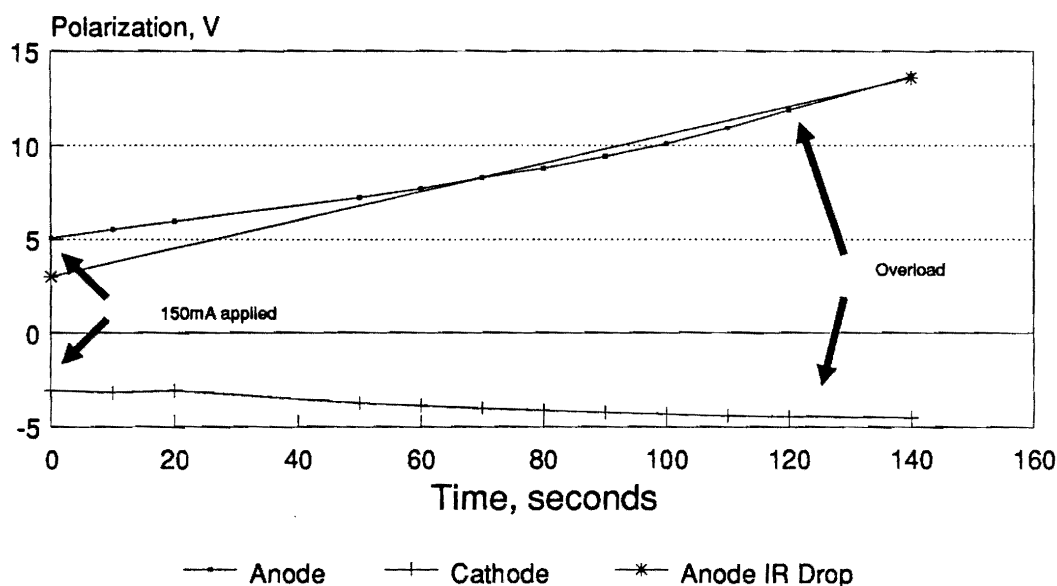
**Figure 21:** Polarization performance of Fibrex electrodes with applied current variations between  $-1\text{ mA}$  and  $0\text{ mA}$ .

large polarization, was on the order of  $13\text{ M}\Omega$ . Housing conductivity was  $0.015\Omega$ , except at the points where the electrode was supposed to come in contact with the housing; resistance readings obtained were on the order of megaohms. The

membrane appeared well wetted, and the seal appeared excellent as the both electrodes and the membrane adhered to the cathode housing when opened. Corrosion and pitting of the 316L housings has been suggested as the cause for the loss of conductivity<sup>3</sup>. While additional avenues are being investigated, it is noted that the housings have oxidized to an appreciable extent.

## Polarization - Run 5

### 150mA applied



Overload, 63.7% stoich removal  
7/2/92

**Figure 22:** Polarization leading to galvanostatic overload at 150 mA.

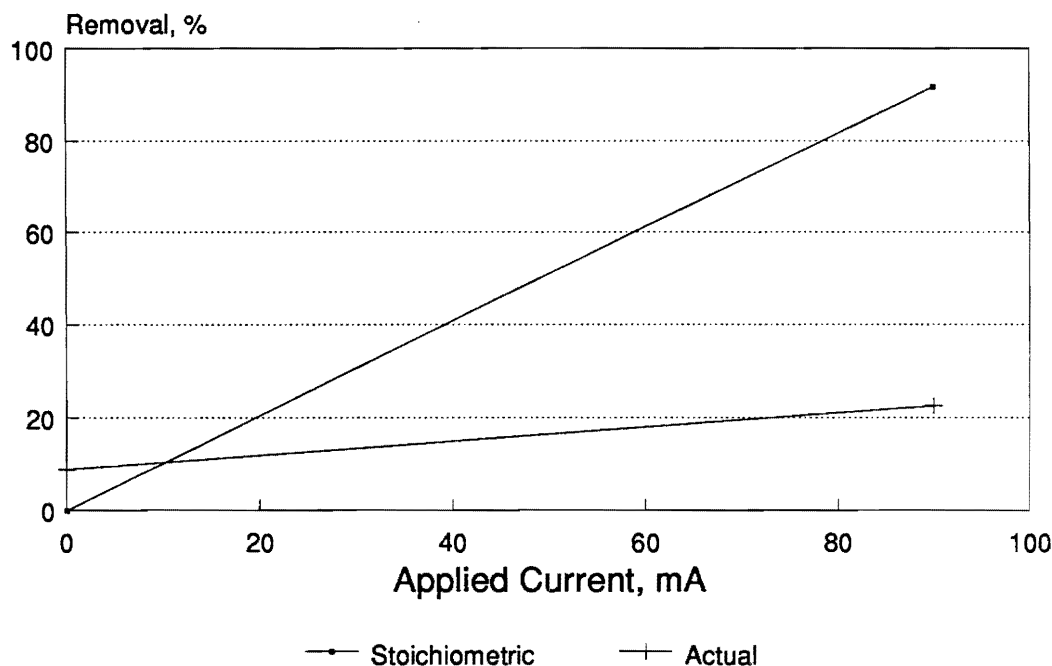
In the attempt to alleviate any short-term conductivity losses, the anode and cathode housings were well cleaned to expose fresh material, and the anode side was painted with platinum paint. Gold wire was also placed between the electrode and the housing on each side to assist in conduction. While the gold withstands the

environment well<sup>4</sup>, excess electrolyte could reduce its effectiveness should the electrode flood and the direct housing-wire-electrode contact be interrupted by electrolyte. Care was thus taken to maintain the minimum amount of electrolyte needed by the cell. Electrolyte addition to the cell was done indirectly through the reference hole.

For verification of the hot-pressed electrolyte/polymer disk viability, the disk was placed above the ceramic matrix and below the cathode electrode. This disk was 33 wt% electrolyte. Other changes in the cell included the use of an 11 vol% ceramic tape for the matrix. The ceramic was the Phillips Petroleum Company Advanced Ceramics experimental powder SC-P. This silicon carbide has a particle size of 0.2 $\mu$ m, and a surface area of 25 m<sup>2</sup>/g. This particle size is ten times smaller than the SN-P particles used in the previous trials. One tape of 11 vol% ceramic was used in this cell. The smaller particles may provide a smaller interstitial pore size. The ceramic was cast in an acrylic binder, available from Metoramic Sciences, Inc. Attempts to cast SC-P in polyvinyl failed at various loading levels of the slurry.

In anticipation of smaller interstitial pore sizes in the ceramic matrix, the E.R.C. electrodes were used in this run, both at the anode and cathode. The 0.75 mm thick E.R.C. electrodes also availed themselves readily to the placement of the gold wire. Both electrodes were lithiated and oxidized prior to use. Upon cell assembly, a crack was heard. It was assumed that one of the brittle E.R.C. electrodes had broken, but to what extent was unknown. Full scale testing continued.

## SO<sub>2</sub> Removal for Run 6



7/12/92

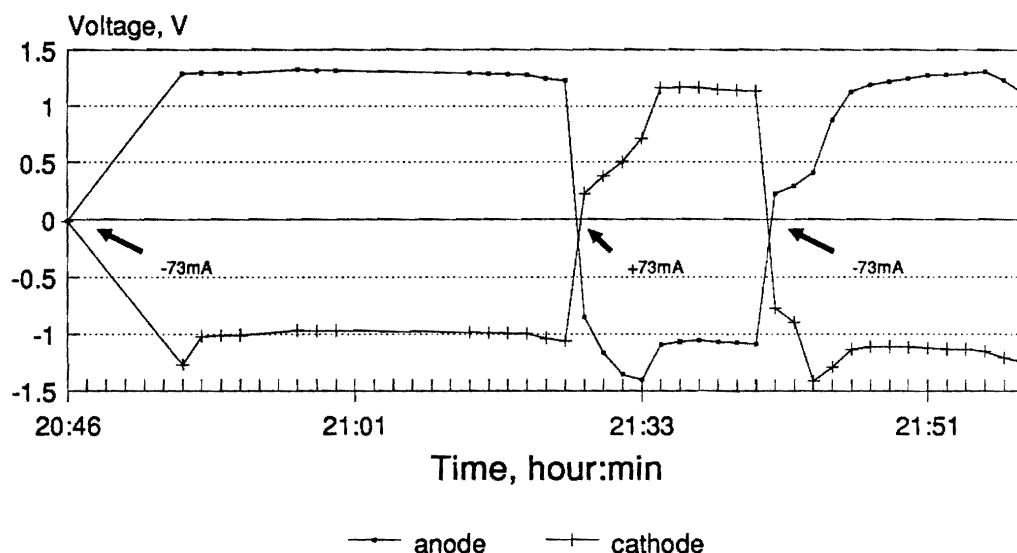
**Figure 23:** SO<sub>2</sub> removal levels versus those of stoichiometric removal at the same applied current.

Due to the large amount of polyethylene oxide in the electrolyte disk in the cell, the temperature ramping proceeded at a slow rate, holding at 275° C for 4 hours under a pure oxygen atmosphere. Upon reaching operating temperature of 400° C, the membrane was noted to have virtually no seal, allowing free gas passage from cathode to anode and the reverse. Removal performance was below stoichiometric as seen in Figure 5, and mass balances did not converge during this run. This was not unexpected, with virtually no seal in the cell; the gas flows and cell reactions could not be properly analyzed.



## Polarization Performance

### Run 6 85.3% Removal



ERC electrodes; 90%K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>/10%V<sub>2</sub>O<sub>5</sub>  
 $i = \pm 73 \text{ mA}$  or 85.3 stoich% removal  
 7/12/92

**Figure 24:** Polarization performance of the E.R.C. electrodes under a varying current of -73 mA to +73 mA.

Polarization performance of the cell was found to be excellent, however. Figure 6 shows excellent response of the electrodes at relatively high current levels. Response indicates that these electrodes might be preferable to the Fibrex electrodes. The total potential of 1.4 V was also excellent and consistent. The run was terminated due to the large crossover and unacceptable removal.

Upon examination of the cell, the ceramic membrane was virtually non-existent. A residue of white powder with electrolyte indicated that the 11 vol% ceramic matrix did not have the density required to maintain a membrane in a cell. In addition, there existed a residue, containing electrolyte, that had flowed out of the

cell, presumably the polyethylene oxide disk. This flow may have led to further degradation of the ceramic membrane, and the lack of sufficient electrolyte in the cell may have added to thermal or mechanical shock absorbed by an unimpregnated membrane.

The electrodes exhibited flooding, similar to that noted by McHenry<sup>2</sup>, and both electrodes were broken, due probably to the force required to separate the cathode and anode housings from one another. The cell was not well-wetted, but there was evidence of an electrolyte path between the anode and cathode electrodes. The perimeter of the cell, however, showed no evidence of an electrolyte presence. Most of the electrolyte appeared to have availed itself to the electrodes and the space in between the electrodes.

### **Electrolyte Management**

It has been found that the 'in situ' placement of electrolyte has led to excellent seals in full scale testing of the SO<sub>x</sub> removal cell. A search has begun for a method of management allowing the placement of electrolyte into the cell prior to binder burnout and cell heating. The presence of the electrolyte is believed to stabilize the ceramic matrix, making it less susceptible to thermal and mechanical shock than an unimpregnated matrix.

The first attempt at this management was the tape casting of the electrolyte in a 78 vol% mixture with polyvinyl binder. The result, reported last quarter, was an inhomogeneous mixture that yielded varying tapes. The slurry itself also

presented difficulties, forming a jelly-like substance that was unmanageable. Only additional solvent allowed the mixture to be poured and cast.

A second attempt to tape cast the electrolyte in a 55.6 vol% mixture with the polyvinyl was made. The slurry was again unmanageable, and only the addition of 30 ml solvent (doubling the total volume) after 24 hours of milling allowed recovery of the slurry. The resulting tape cracked and adhered to the casting surface.

Attempts were then made to cold and hot press a disk of pure electrolyte. The cold-press was carried out with 2.5 g electrolyte and 1050 psig for 5 minutes. The resulting disk was fragile and crumbled to the touch. Subsequent attempts at pressures of 1680 psig and 10 minutes produced the same results.

The hot press technique is somewhat arbitrary in this application. The presence of bisulfates in the pyrosulfate exposed to humidity greatly reduced the melting point; while bisulfates will melt and decompose to pyrosulfate upon heating, that melting is not desirable in the hot pressing process. Hot pressing requires pressing the material at a point 10-15° C below its melting point. If that melting point is not well known, the procedure will tend to be ineffective. The melting point of the electrolyte was determined to be approximately 300-350° C, and a pressing temperature of 275° C was chosen. Three times, the die was baked in the oven for 5-10 minutes, and then pressed at 1050 psig for 1 minute. The resulting disk, while showing a slightly stronger mechanical strength than the cold pressed disk, still fell apart during handling.



Polyethylene oxide was first milled with electrolyte for a minimum of 1/2 hour before placement between two cut aluminum foil circles in the pressing die. The die was then alternated between an oven and the press, for various numbers of cycles and at various temperatures. Pressing occurred at 1900 psig in all cases. This technique was tried with two different molecular weights of polyethylene oxide: 900,000 and 100,000. The results are shown in Table II. Also shown in Table II are the results of the use of hydroxyethyl cellulose, courtesy Union Carbide Corporation, in combination with the electrolyte. The hydroxyethyl cellulose has been shown to burn out completely at a temperature of 350° C. Work has just begun on a hot pressing technique with hydroxyethyl cellulose. Up to this time, the cellulose has been cold pressed only, also at 1900 psig.

Future work in electrolyte management will include the development of tape casting techniques, should the pressed-disk methods proved unsatisfactory or inconsistent. Preliminary results have shown that for the same mixtures and processing, two very different disks can be obtained. Method must be improved if this type of processing is to prove to be viable. Tape casting of the electrolyte and ceramic matrix is a relatively well-developed method of electrolyte management in the molten carbonate fuel cell<sup>5,6</sup>, and will be considered as an option, should it be found that the addition of electrolyte will not increase the interstitial pore size of the ceramic matrix.

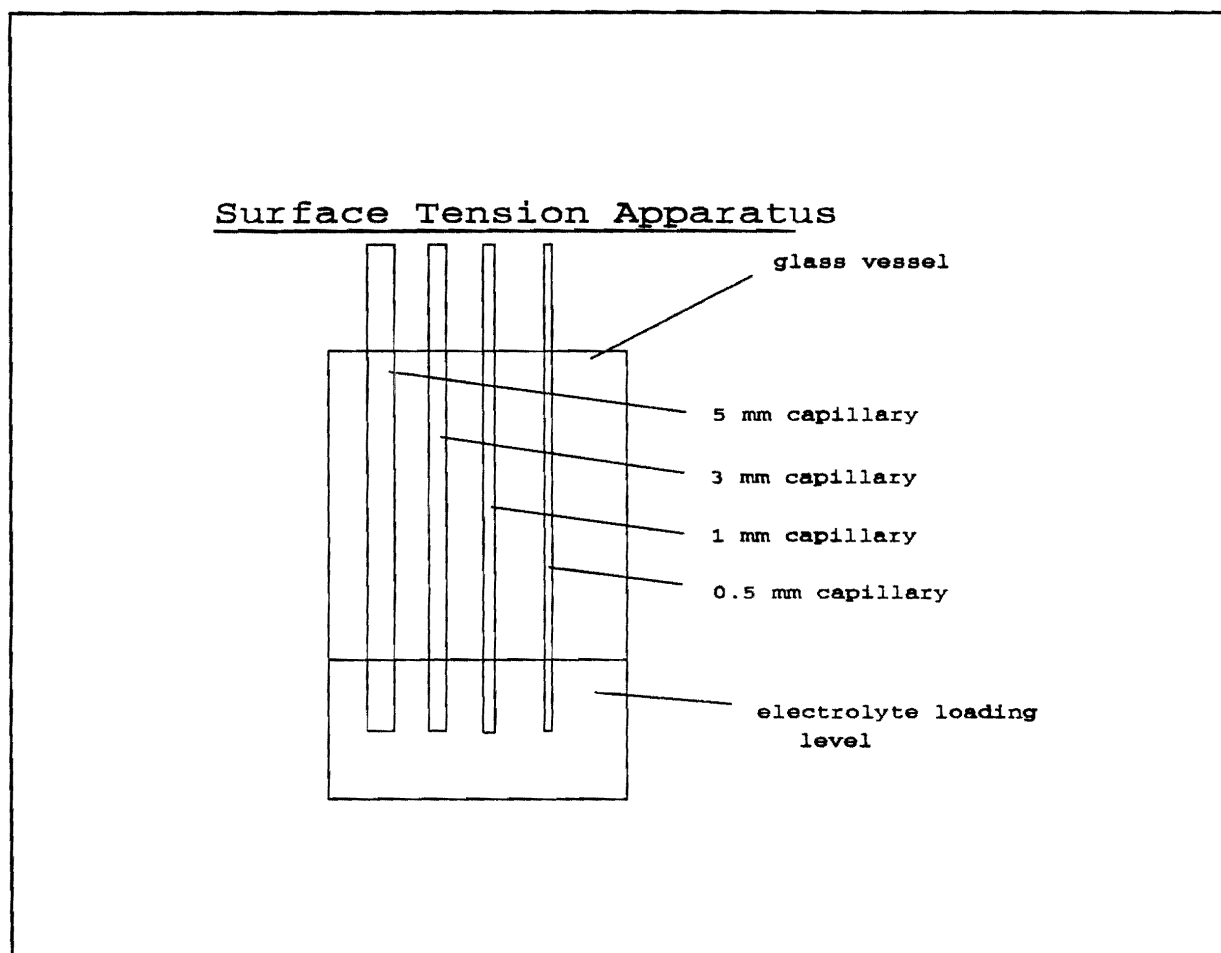
### **Electrolyte Experiments**

Before any type of model for electrode wetting can be developed, the transport properties of the molten electrolyte must be known. While much data is available for potassium sulphate, little is known about potassium pyrosulfate, and even less about a mixture of potassium pyrosulfate and vanadium pentoxide. An experiment was performed to determine the density of the molten salt at 400° C.

A Pyrex graduated cylinder was used to determine the density. The coefficient of linear thermal expansion for Pyrex is listed as  $0.033 \times 10^{-6}$  up to 300° C. The expansion of the cylinder due to the increase in temperature was therefor assumed negligible. The cylinder was loaded with a known weight of electrolyte, covered to maintain a constant SO<sub>3</sub> partial pressure, and heated. Readings were taken over a 4 hour period. The loss of weight was found to be 0.083 g  $\pm$  0.005 g possibly due to SO<sub>3</sub> formation or vaporization of any water present on the surface of the cylinder. This small loss was considered negligible. The beginning and end weights were averaged, and the density at 400° C was calculated as 1.997 g/ml  $\pm$  0.05 g/ml. Error in this experiment may result from an inaccurate reading, or solidification of the molten salt when the oven was open to read the height.

An attempt was then made to calculate the surface tension of the electrolyte using capillary tubes (see Figure 7). The Pyrex housing was marked at known

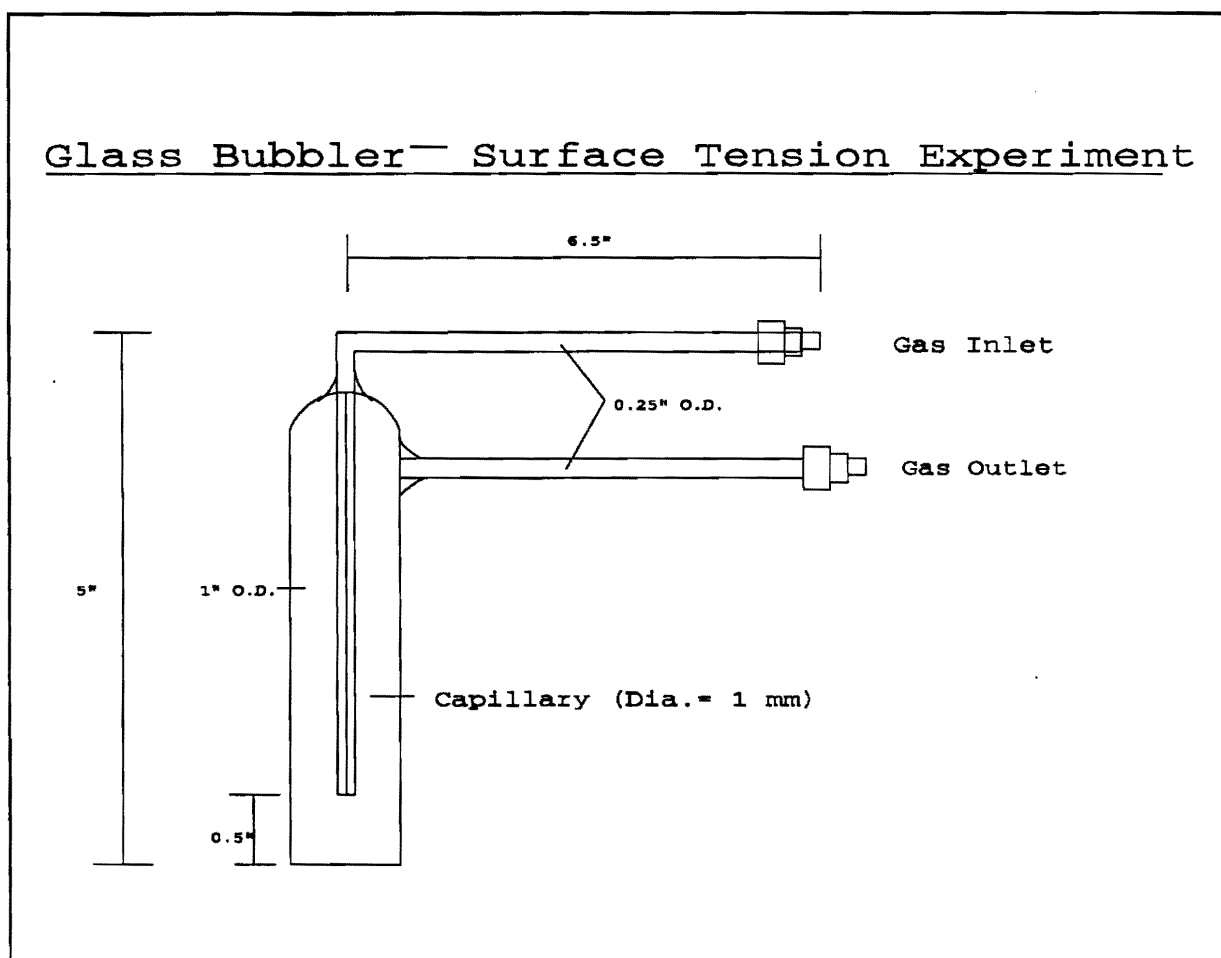
$$\gamma = \frac{r h \rho g}{2} \quad (6)$$



**Figure 25:** Capillary apparatus used in an attempt to determine the surface tension of molten electrolyte.

intervals for visual height measurement. The capillary tubes used were of inner diameter 5 mm, 3 mm, 1 mm, and 0.5 mm, and also of Pyrex. The multiple tubes eliminated the absolute need to know the height of the molten electrolyte in the housing. Using the capillary equation (6), and taking the differences in height for the different size capillaries, the surface tension could be determined independently of the height of the molten electrolyte.

The result, however, was not readable. Electrolyte level was only readable in the 0.5 mm capillary; the larger ones all had plugs of electrolyte at various levels,



**Figure 26:** Bubbling apparatus for use as described in Jaeger's maximum bubble pressure method.

leading to the questioning of the validity of any reading with the slight partial pressure differences that must exist between plugs of electrolyte. The level of the molten electrolyte was measure in the housing and in the 0.5 mm capillary. From these readings, a reading of 93.69 dynes/cm  $\pm$  6.85 dynes/cm at 400° C was obtained.



Lovering<sup>8</sup> has suggested Jaeger's<sup>9</sup> maximum bubble method as an excellent technique with which to measure the surface tension of a molten salt. The method

$$p = \rho gh + \frac{2\gamma}{r} \quad (7)$$

requires the ability to measure the pressure required to force one N<sub>2</sub> bubble out of an opening at a known depth. This pressure is assumed to be due to the depth of the liquid and the force required to overcome the surface tension of the liquid, forming a bubble. The equation used is shown as Equation (7), where p=pressure, h=depth of immersion for tip of capillary, r=radius of the capillary opening, g=gravitational constant, ρ=density of the melt, and γ=surface tension. An apparatus was then developed for the experiment (see Figure 8), and a mercury manometer was used to measure the pressure difference.

The result is encouraging, although the range is large. The manometer read only a 6 mmHg difference. The pressure reading is the largest source of error, and was treated as such in the analysis. The final value for surface tension from the maximum bubble pressure method was 138.8 dynes/cm ± 33.4 dynes/cm. The two values stand almost in agreement with one another, yet neither is felt to have the desired accuracy. In the next attempt to measure the surface tension, the Hg manometer will be replaced with a H<sub>2</sub>O manometer for accurate pressure measurement. In addition, SO<sub>2</sub> and SO<sub>3</sub> will be bubbled through as well as N<sub>2</sub>. This

may aid in allowing the electrolyte to maintain a constant  $\text{SO}_3$  partial pressure, although this is not a major concern.

### **Ceramic Membrane Development**

Various schemes have been tested this quarter in an attempt to develop a ceramic membrane with a pore size less than  $0.2\mu\text{m}$ . Phillips Petroleum Silicon Nitride, SN-P, had been used in previous runs, and found by McHenry<sup>2</sup> to have an interstitial pore size of  $0.2\mu\text{m}$ . Smaller pore sizes would enable the use of the E.R.C. electrodes, which flood when used with a SN-P membrane. Tape casting, as described previously has been the method of membrane manufacture, allowing the development of 0.30 mm membranes for used in full scale testing.

Attempts have been made to develop a membrane using particles with a diameter ( $d_p$ ) of  $0.2\mu\text{m}$ , an order of magnitude smaller than SN-P particles. Phillips Petroleum SN-R, a silicon nitride, and SC-P, a silicon carbide, have both been considered. Both have  $d_p=0.2\mu\text{m}$ . The binders available at this time are provided by Metoramic Sciences, Inc.: B73305, a polyvinyl, and K565-4, an acrylic. Modifiers for casting on glass (M-1111) and galvanized steel (M-1114) are also available. The results of various attempts can be seen in Table III. The one SC-P membrane that did cast (#3, Table III) was used in Run 6, and was shown to have inadequate ceramic volume to maintain the matrix. A higher volume percentage ceramic is needed.

Future membrane work includes the development of a tape casting technique for the SN-R and SC-P particles. At this point, there are various combinations to still

**Table III: Ceramic Tape Casting**

#	Ceramic	Vol% ceramic	Binder	Modifier	Results
1	SN-R	50.0	Vinyl	M-1114	Would not flow despite sonication
2	SN-R	48.3	Vinyl	M-1114	Additional solvent; cracked upon drying
3	SC-P	11.0	Acrylic	M-1111	Cast well; pliable tapes
4	SC-P	50.0	Acrylic	M-1111	Did not cast well; cracked upon drying
5	SC-P	30.0	Acrylic	M-1111	Not homogenous; cracking
6	SC-P	40.0	Acrylic	M-1111	Cracked on drying

be tried, and new binders must also be considered. A membrane of approximately 50 vol% ceramic is desirable, although a more dense membrane will also be considered. Less dense membranes do not have the physical ability to maintain the matrix.

### **Future Research**

The E.R.C. electrodes have demonstrated excellent polarizability. Before they can be used, however, a ceramic matrix with a smaller interstitial pore size must be developed. The development of an electrolyte membrane has proven to be crucial in consistently developing and maintaining gas seals.

It is also crucial that a full scale test exhibit converging mass balances to verify results from previous runs. A working full scale test with the new materials is also needed to see the effect of new materials on the problem of SO<sub>2</sub> generation.

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**Quarterly Progress Report:**  
**High Temperature Membranes for**  
**H<sub>2</sub>S and SO<sub>2</sub> Separations**  
**Grant DE-FG22-90PC90293**  
**July 1, 1992 - September 30, 1992**

**by**

**Professor Jack Winnick**  
**Georgia Institute of Technology**  
**School of Chemical Engineering**  
**Atlanta, Georgia 30332-0100**



## Purpose and Goals of Research

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen which enriches the syn-gas, and sulfur which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  cell and the  $\text{SO}_2$  cell require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies, or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress towards these goals.

## I. SO<sub>x</sub>/NO<sub>x</sub> Removal Cell

### Introduction

Successful removal of NO<sub>x</sub> and SO<sub>x</sub> from flue gas depends on the development of a membrane able to achieve a current density of 50 mA/cm<sup>2</sup> at a total voltage of approximately 1V. Flooding of electrode has been identified as a problem, leading to increasing polarization over time. The resulting reduction of surface area also tends to limit the mass transfer flux, reducing the efficiency of the cell. To reduce flooding, new materials and techniques of manufacture will be investigated, in the attempt to produce a ceramic membrane of approximately 50% theoretical density. This membrane must have proper pore size distribution to ensure sufficient capillary force to prevent impregnated electrolyte from flooding electrodes, and subsequently drying the ceramic membrane.

Electrolyte introduction to the cell is a continuing problem. The development of a method is still being investigated. Ideally, the electrolyte would be introduced as powder with binder in a green body. This binder would ideally burn away at temperatures of approximately, leaving pure electrolyte to melt and complete the salt bridge necessary for the electrochemical cell. The electrolyte used this quarter was, exclusively, a 90wt%K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>/10wt%V<sub>2</sub>O<sub>5</sub> mixture.

Electrodes used this quarter were lithiated nickel oxide. These were obtained from National Standard and the Energy Research Corporation (E.R.C.) as Ni sheets.

These sheets were cut, with a resulting superficial area of approximately 20.0cm<sup>2</sup>. The cut Ni was placed in a 1-2M solution of LiOH, dried, and oxidized at 600° C prior to placement in the cell. This process creates a p-type semiconductor, exhibiting room resistivities on the order of 0.2Ω at room temperatures. Pore size of the National Standard Fibrex electrodes is approximately 1.0 μm. The pore size of the ERC electrode is proprietary.

Current is conducted through the cell from stainless steel 316L housings, to the electrolyte-wetted electrode, where the removal takes place. The current is then carried through the cell by the transporting species in the electrolyte. Oxidation of the transporting species occurs at the anode, and the current passes through the anode electrode to the anodic SS316L housing, and out of the cell.

#### **SO<sub>x</sub> REMOVAL:**

#### **Summary**

Attempts to use polyethylene oxide as an electrolyte binder last quarter were evaluated for material properties and reactions. In addition, the effects of the solvents used in tape casting techniques were evaluated with electrolyte for any reaction that might occur. These evaluations utilized the technique of x-ray diffraction. For this technique, materials to be analyzed must be in solid phase at room temperature, and

have low vapor pressures. Furthermore, organic material such as waxes or greases will not be "seen" by this technique.

A  $\text{ZrO}_2$  mat, obtained from Zircar Fibrous Products, was tested and evaluated for its use as a ceramic membrane. Testing involved the evaluation of the mat after 24 hours exposure to the electrolyte at  $400^\circ \text{C}$ . Also involved was a full-scale test of the mat in removal cell. Post mortem x-ray diffraction results are discussed.

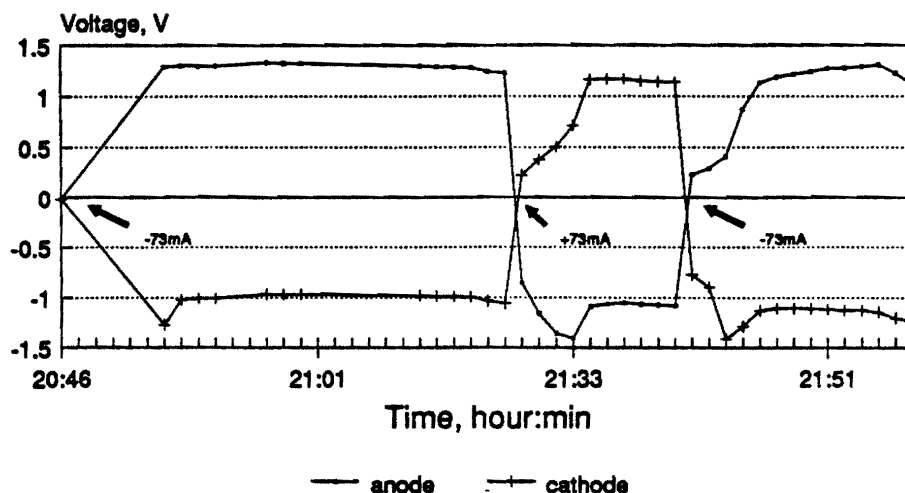
$\text{NO}_x$  removal capabilities were also studied in some depth this quarter. A possible mechanism for the anodic removal is proposed, based on a one electron transfer mechanism. The results of full scale testing and the theoretical diffusion limited current will be compared. Results at this point show excellent fluxes, but poor current utilization based on the present scheme.

## Results

A tape cast membrane of 11.1 volume percent "B" ( $\text{Si}_3\text{N}_4$  of  $0.2\mu\text{m}$  particle diameter) was used in a full scale test run. The electrodes used in this run were obtained courtesy E.R.C. Corporation. The interstitial pore size of the resulting "B" membrane would be small enough to prevent flooding of the E.R.C. electrodes. The performance of the E.R.C. electrode in past experiments has suggested that their use in full scale removal systems would be beneficial. The anode side was covered with Pt paint and gold wire was laid length-wise across the electrode in an attempt to ensure non-corroded contact with the housing, and no resistance to current passage from the

housings. The cathode side was well cleaned. Burnout of the polymer binder took place under an oxygen atmosphere, and electrolyte was added to the system after burnout at a temperature of 350° C.

## Polarization Performance Run 6 85.3% Removal

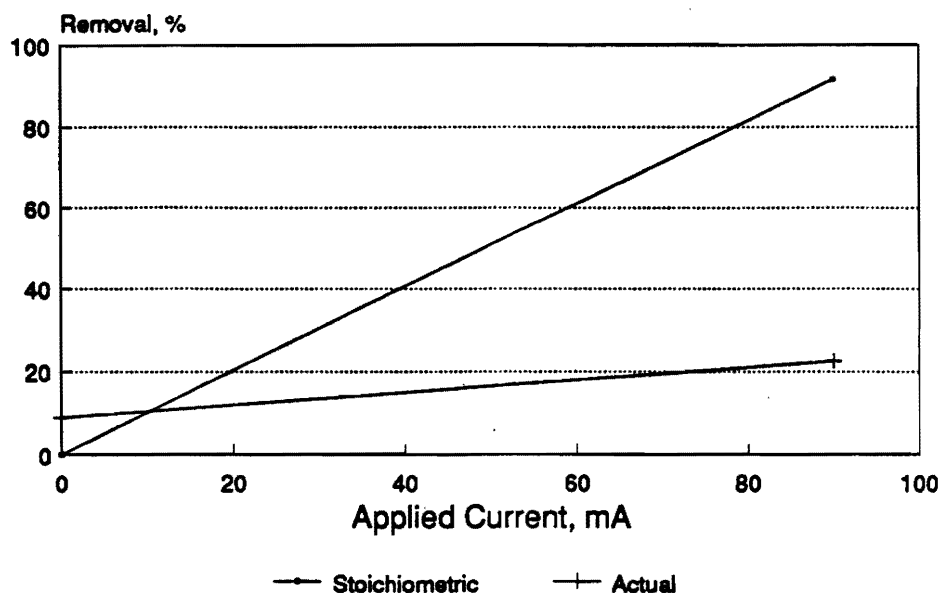


ERC electrodes; 90%K2S2O7/10%V2O5  
I<sub>app</sub> = 73mA or 85.3 stoich% removal  
7/12/92

Figure 1: Polarization performance with a 25vol% "B" membrane.

Gas crossover was checked as the temperature reached 400° C, and was found to be substantial, at 5-10 1 cm diameter bubbles per sec in 1 mmH<sub>2</sub>O, with a gas flow rate of 220 cc/min. The cell exhibited good polarization characteristics (see Figure 1). Potentials across the cell were also found to be substantial, with an overall cell potential of 2.5 V with an applied current of 73 mA. Removal was found to be poor, around 60% with 100% stoichiometric current applied (see Figure 2), and removal mass balances did not balance. In light of these conditions, the cell was shut down.

## SO<sub>2</sub> Removal for Run 6



7/12/92

**Figure 2:** SO<sub>x</sub> removal using a 25vol% "B" membrane.

Post mortem analysis showed the problem to be the non-existent membrane. Evidence suggests that upon burnout, the volume percentage of ceramic in the tape was not high enough to support itself, and dissolved in the electrolyte, allowing the free passage of gas from one side to another. The absence of membrane would explain the effect noticed, and thus, the failure of the cell was attributed to it. The search for a more densely packed membrane, exhibiting, ideally, a small interstitial pore size with a void volume of 50%, continues.

A 25 volume% "B" membrane was constructed. This time, two membranes were placed together, forming a thick green membrane of 0.91 mm thickness. Electrolyte introduction was attempted in a pressed disk of hydroxyethyl cellulose/electrolyte, 80% electrolyte by weight. Fibrex electrodes were used, in an attempt to conserve E.R.C.

electrode material. Gold wire was again used across the electrodes on each side to aid in housing to electrode conduction, with a measured resistance of  $0.2\text{--}0.9\Omega$  ( $25^\circ\text{C}$ ) on each side prior to cell start-up.

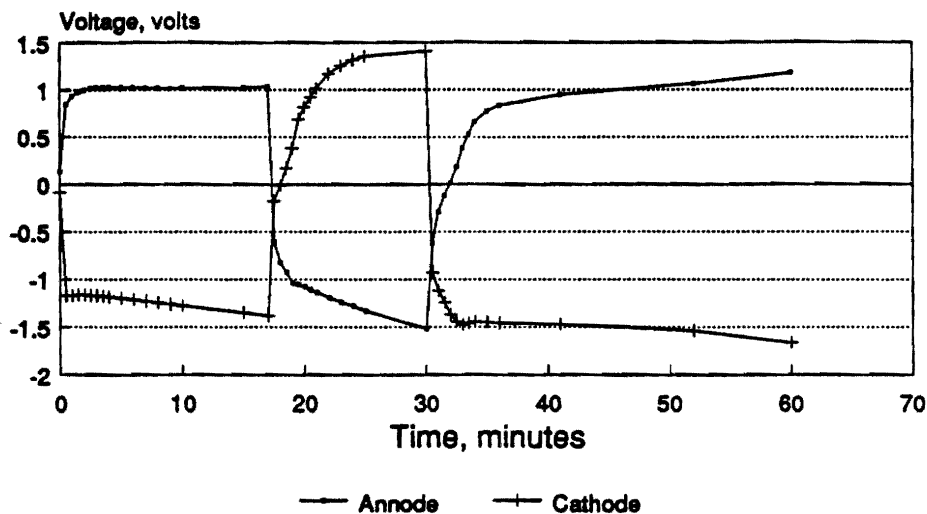
This run again exhibited a large crossover, rendering the run useless. Additional electrolyte was added in an attempt to alleviate the crossover, to no effect. Power failure to the building necessitated the shutdown of the run. Upon breakdown, it was noted that the electrolyte had not wet the ceramic membrane fully, probably leading to the detected crossover. Resistance measurements showed a housing to electrode resistance of  $0.2\text{--}0.8\Omega$  on the cathodic side, and  $4\text{--}9\Omega$  on the anodic side. This increase in resistance was startling.

In response to the failure, a run was again attempted with a two 25.9vol% "B" membranes pressed together, with a total thickness of 0.29 mm. Again Fibrex electrodes were utilized, along with gold wire for conduction. The housings were thoroughly cleaned prior to use.

The cell exhibited crossover, with possible leakage out the side. Additional electrolyte was added, and the crossover and leakage problems were eliminated for a very short time. The cell suddenly seemed to "pop," however, as the crossover again started, although cell leakage decreased dramatically. Cell testing continued.

Polarization of the cell showed an excellent response to current (Figure 3), with  $iR$  drop showing a linear current response (Figure 4). The limiting polarization is believed to occur due to the formation of sulfate on the surface of the electrolyte/electrode interface, reducing the area available for mass transfer, and thus

## Polarization 95cc/min Flue Gas Run 8



+/-35mA=95stoich% T=400C  
8/12/92 DS

Figure 3: Potential response to current applied to the cell.

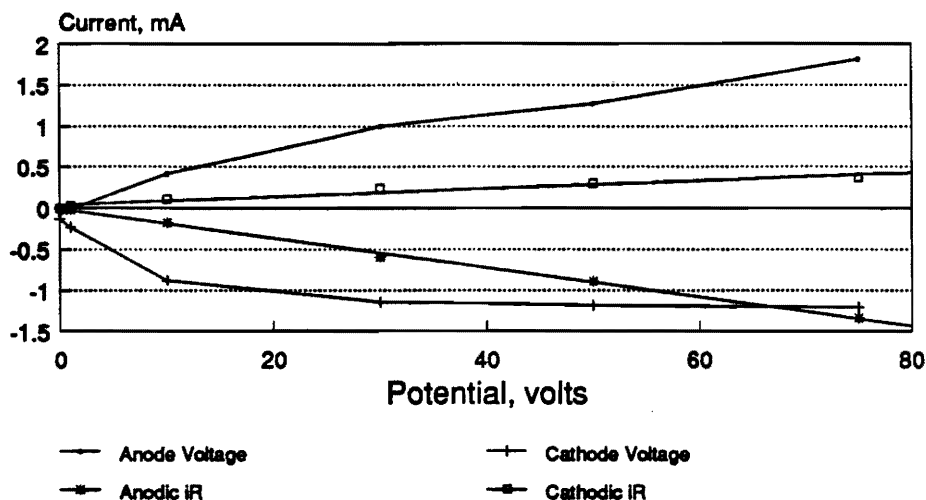
increasing the resistance to transport.

This polarization response, corrected for  $iR$ , was then graphed as seen in Figure 5. The limiting current occurred at the approximate point of stoichiometric current. This suggested that the system response to current was stoichiometric, but removal remained poor at approximately 45%. Crossover is the probable reason for such poor removal. The limiting potential may have also been caused by diffusion limitations in the gas stream.

Breakdown of the cell showed that only 90% of the membrane was wetted, and gas leakage was suspected to occur in the dry region. Once again, the anodic housing to electrode resistance ( $3.5\text{--}5\Omega$ ) after breakdown was higher than that of the cathode ( $<1\Omega$ ). The gold wire seems to have some effect, as large resistances are not seen, but



## Polarization Series Run 8



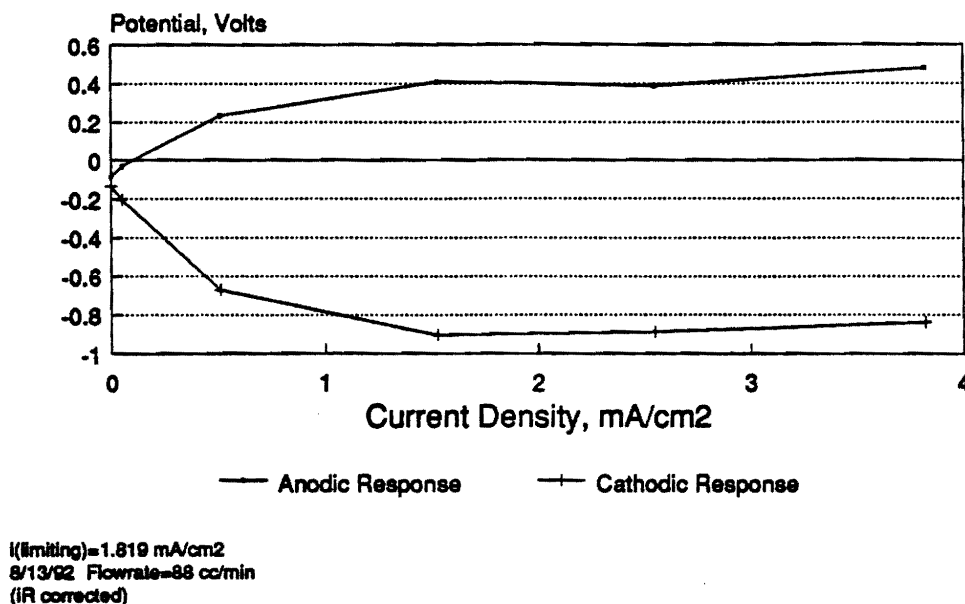
Flow=89 cc/min,  $i(\text{limiting})=35.7\text{mA}$   
8/13/92

Figure 4:  $iR$  and potential response to applied current.

the problem with increases in resistance on the anodic side still persists. The gold wire fused to the housing to an extent, and was also frozen in electrolyte. electrolyte may have wicked between the gold wire and the electrode. Sulfate formation from the pyrosulfate equilibrium may impede the current path, resulting in a high resistance.

Increasingly, the formation of a lavender color on the anode electrode has been noticed post-mortem. This color is predominate on the electrode in the region where it came into contact with the housing, and was observed to extend onto the housing in areas where the electrode came into contact. This color change may indicate the formation of a chromium (III) sulfate, which is known to exhibit a lavender color<sup>1</sup>. Other possibilities include, but are not limited to  $\text{CrO}_3 \cdot x\text{H}_2\text{O}$  or  $\text{Mo}_2\text{O}_5$ . Various other complexes are being researched, including pyrosulfate complexing, vanadium complexes,

## Polarization Run 8



**Figure 5:** iR corrected polarization response of the cell to current applied.

and other metal complexes.

X-ray diffraction performed on an 80wt% electrolyte 20wt% hydroxyethyl cellulose disk after exposure to the atmosphere at 400° C showed the formation of multiple phases, with little to no potassium pyrosulfate detected. Reaction depletion of the pyrosulfate occurred. In addition, electrolyte was dissolved in an 80%/20% ethanol/toluene solution at 25° C. This solution is the solvent used in the polyvinyl binder system discussed in earlier reports. The solution was dried with low heat, and filtered. X-ray diffraction, performed on the resulting solid, showed, again, a reaction had taken place. This result was expected, as pervious attempts to use the polyvinyl binder system had resulted in unusable material and membranes.

## Future Work

The inability to tape cast a 50% dense membrane with the smaller "B" particles has led to the attempt to sinter such a membrane. Literature suggests that pure  $\text{Si}_3\text{N}_4$  cannot, in fact, sinter to more than a 50% theoretical density. Usually, additives such as ceria and yttria are used to obtain a 100% dense membrane. Yttria and ceria have been shown by McHenry<sup>2</sup> to react with the removal system, and thus are not desired. A 50% theoretically dense membrane is desirable in this case. A sintering temperature and rate must be theoretically determined. Theoretically, a thick 2mm membrane will be cast, under a pure  $\text{N}_2$  atmosphere, and will then be sanded down to the desired thickness.

Mechanical stability is a major concern, and mechanical and thermal shock to the membrane must be minimized. Preliminary results indicate that a hard, mechanically strong structure can be obtained. It has also been found that  $\text{Si}_3\text{N}_4$  will react with alumina. At the present time, BN (boron nitride) and  $\text{Si}_3\text{N}_4$  are being researched as non-reacting systems on which to fire the disk. Further findings will be presented in future reports.

## $\text{NO}_x$ STUDIES:

Theoretical as well as experimental studies on the removal of  $\text{NO}_x$  from flue gas have been performed this quarter. The results are promising, although, again, the need for a suitable membrane is crucial to the success of the removal system.

## Introduction

Large coal and natural gas reserves in the United States have led to the development of a large coal-based power industry. Various coal and natural gas combustion products, however, have been found to be harmful to both the environment and to humankind. Particularly, the oxides of nitrogen, which can react to form acid rain, are of great concern, and their emission is regulated. Conventional technology for the control of  $\text{NO}_x$  emissions uses low  $\text{NO}_x$  burners, which require precise control of air and recycle streams, and has proven to be expensive in the low ppm range. The electrochemical membrane process suggested here is a polishing application, although it has been shown to exhibit excellent removal at higher concentrations.

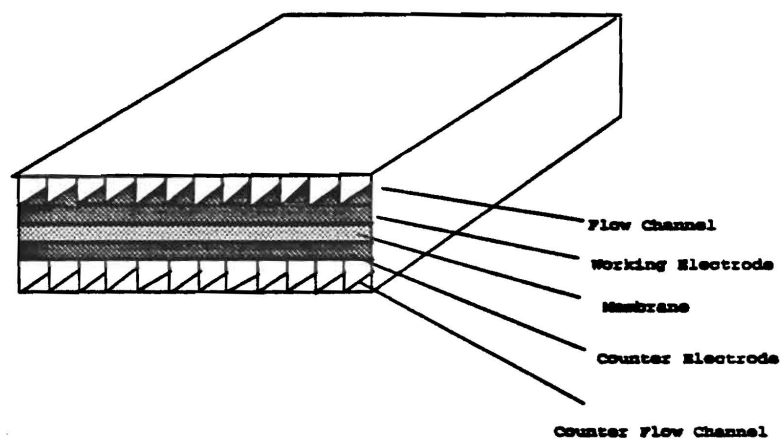
The control of  $\text{NO}_x$  emissions has been discussed throughout the industry. There have been two distinct fields of thought developed: one field condones removal after the burning process, and one wants the control of emissions taking place at the burning process. The control of the percentage of air to the burner has been shown to have marked effects upon the level of nitrogen oxides in the flue stream<sup>3</sup>The retro-fitting of many burners with low  $\text{NO}_x$  burners has reduced the emissions through the use of a less turbulent air-fuel mixing zone, reducing the availability of oxygen and reducing  $\text{NO}_x$  formation. However, as the technology for control of these operations has pushed forward, the cost has increased<sup>4</sup>. In addition, a low- $\text{NO}_x$  burner with fuel staging still reduces emissions by only 80%.

Downstream removal of the gas has been traditionally carried out by the selective non-catalytic reduction of ammonia, at temperatures of approximately 870-1100° C<sup>5</sup>. While an 80% reduction may be achievable, the high temperatures involved greatly increase the cost and hazard involved. A selective catalytic reduction method, using a catalyst such as vanadium or platinum, will operate at lower temperatures (375-400° C), but the rapid degradation of the costly catalyst increases the expenses of this process.<sup>5</sup> Removal is once again on the level of 80% or better.

Electrochemical process have the distinct advantage of the efficient use of energy for the direct removal, transport, or decomposition of products. The upper limit of 35-40% efficiency of Carnot-type cycles is the minimum efficiency for the practical electrochemical cells. The theoretical free energy efficiencies for electrochemical cells is approximately 100%, while free energy efficiencies actually obtained are on the order of 60-80%<sup>6</sup>. Other advantages of the use of electrochemical cells are the virtually non-existent side products from well-developed systems. These include low noise pollution (no mechanical parts excepts for pumps and compressors where needed), little thermal pollution in its efficient energy usage, and a relatively small footprint, electrochemical cells can be used in virtually any environment and under various conditions.

The electrochemical process envisioned contains two stacks of electrochemical cells, each removing 90% of the incoming pollutant (thus 99% removal with two stacks) at a temperature of 400° C. Each stack (see Figure 6) would consist of a series of electrochemical cells, stacked one upon the other separated by bipolar plates and flow channels, much in the same manner as the manufacture of the Molten Carbonate Fuel

### Cut-Away of Flow Channels



**Figure 6:** Model Molten Carbonate Fuel Cell electrochemical stack.

Cell (MCFC). Each electrochemical cell would consist of a ceramic matrix which would be impregnated in situ with electrolyte. Lithiated nickel oxide porous electrodes will be placed on both sides of the electrolytic matrix. Flow channels would be located above each of these electrodes to allow the gas stream to contact the electrolyte through the porous material. A bipolar plate would separate one cell from its two neighbors. Each cell would be approximately 0.53 cm in height, and 1.5 m in width and length (see Figure 6). In the presented process, the gas containing the  $\text{NO}_x$  flows past the anode, where it is decomposed into oxygen at the anode and nitrogen at the cathode. The captured species is believed to be a vanadium complex, which is transported across the membrane to the cathodic side, where it forms nitrogen, and is removed from the cell by a sweep stream of. The exiting streams are thus virtually  $\text{NO}_x$ -free.

## Theory

The selective removal of  $\text{NO}_x$  from flue gas can be accomplished through the decomposition of  $\text{NO}_x$ , and the transport of a vanadium complex across a membrane. The decomposition and resulting transport requires a driving force. This driving force will be electrochemical.

Most membrane processes require a pressure gradient or mass gradient as the driving force for removal such as filtration and osmosis. To accomplish these removals, the process must overcome a chemical potential gradient:

$$\Delta \mu_i = \mu_i - \mu'_i = RT \ln \left( \frac{a_i}{a'_i} \right) \quad (1)$$

where the activities of component  $i$  in each phase separated by the membrane is denoted by  $a_i$  and  $a'_i$ . High pressures are usually required to overcome osmotic or partial pressures, and removal is not necessarily highly selective.

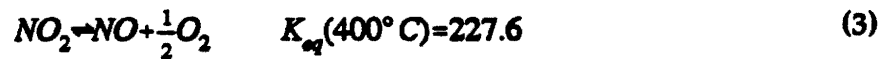
If a species is a strong electron donor or acceptor, it can be preferentially removed through its ionization in electrolyte, and transport through the electrolyte. For a species with a net charge  $z_i$ , and a potential difference across the membrane of  $\Delta \Phi$ , the driving force must exceed the electrochemical potential:

$$\Delta \bar{\mu}_i = \bar{\mu}_i - \bar{\mu}'_i = RT \ln \left( \frac{a_i}{a'_i} \right) + z_i F \Delta \Phi \quad (2)$$

Using an electrochemical process, a highly selective and energy efficient removal can be accomplished with virtually no side effects.

The  $\text{NO}_x$  present can act as a strong Lewis base in our system. The reaction is believed to follow the proposed pathway:

$\text{NO}_2$  present in the system can be converted to  $\text{NO}$  as seen in Equation (3)<sup>7</sup>.

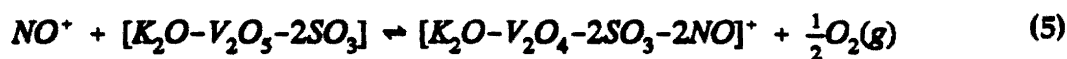




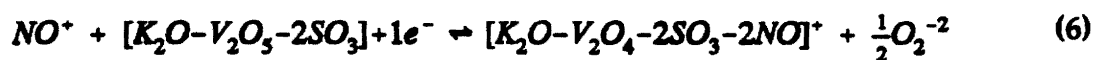
Bontempelli<sup>8</sup> studied the effects of nitrogen oxide oxidation in concentrated sulfuric acid. He suggests NO from the gas stream can be oxidized through current



As NO is consumed through Equation (4), the partial pressure of O<sub>2</sub> increases, increasing the solubility of O<sub>2</sub> in the electrolyte, but limiting the extent of equilibrium in Equation (3). While the exact transport mechanism is not known, the solvated NO<sup>+</sup> could then complex with vanadium present in the molten pyrosulfate as alluded by Franke<sup>9</sup> and McHenry<sup>10</sup>:



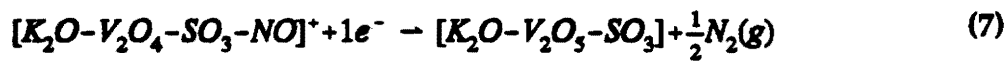
The alternate to this type of complexing is the formation of a peroxide species in the melt. Many authors<sup>11,12,13,14,15</sup> have suggest the presence of peroxide at high temperatures, and the complex reaction may be as seen in Equation (6):



If Equation (6) is the method of complexing, NO<sup>+</sup> would become the species migrating to the cathode interface, where it could form the peroxide. The peroxide would then transport back to the anode. The complex formed would remain at the cathode, where

reduction would occur. This reaction, however, would require additional current for the complete system reaction. Because the extent of this possibility is unknown, this reaction will not be considered in the overall evaluation.

The complex formed in Equation (5) is then transported across the cell to the cathode, where it can take place in the chemical reduction of the species as seen in Equation (7)



where the gaseous  $N_2$  diffuses into the cathodic sweep stream for transport out of the cell.

The overall cell reaction, a one electron transfer redox reaction, is then found by the addition of Equations (4), (5), and (7) to be:



the decomposition of nitrogen monoxide at  $400^\circ C$ , where the gibbs free energy of formation was determined from JANAF<sup>16</sup> tables.

To produce decomposition in this cell, the ability of the current supplied to force the desired reactions must be maximized. While increasing the contact time of the species to be decomposed will allow a higher percentage of removal, some optimum must be achieved between the contact time, the current efficiency, and most importantly, the cost.

To determine the limit of the electrochemical decomposition, the limit of each removal step must be examined. These steps are as follows:

1. transport of  $\text{NO}_x$  from the bulk stream to the gas/electrolyte interface;
2. electrolysis of electrolyte to form the transporting species at the anode;
3. ionic transport across the membrane;
4. electrolysis of the transporting species to cathodic product species;
5. transport of cathodic product species to the gas sweep stream.

The development of a system for the removal of  $\text{NO}_x$  must make assumptions to determine the best available removal. The major assumption is that, at steady-state with efficient current usage, steps 2 through 5 are not limiting. The limiting step in the system is therefore the ability of the  $\text{NO}_x$  to transport from the gas stream to the gas/electrolyte interface for the reactions to occur.

The main mechanism for transport of the gas-phase species to the gas/electrolyte interface, in a laminar system, is the ability of the species to diffuse through the transporting medium, assumed to be primarily nitrogen.

Gas phase diffusivity has been fairly well defined through the use of molecular models. Welty, Wicks and Wilson<sup>17</sup> suggest Equation (9) for non-polar, non-reacting molecules,

$$D_{AB} = \frac{0.001858 T^{\frac{3}{2}} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{\frac{1}{2}}}{P \sigma_{AB}^2 \Omega_D} \quad (9)$$

where  $D_{AB}$  is the mass diffusivity of A through B in  $\text{cm}^2/\text{sec}$ ;  $T$  is the absolute temperature in degrees Kelvin;  $M_i$  is the molecular weight of component  $i$ ;  $P$  is the absolute pressure in atmospheres;  $\sigma_{AB}$  is the Leonard-Jones collision diameter in Angstroms, and  $\Omega_D$  is the collision integral, a function of Leonard-Jones parameters and the temperature. At  $400^\circ \text{C}$ , the diffusivity of NO (A) through  $\text{N}_2$  (B) is  $0.8336 \text{ cm}^2/\text{sec}$ .

This diffusivity can then be related to a mass transfer coefficient ( $k_m$ ) through the Nusselt number ( $N_{Nu}$ ), for a given hydraulic diameter as seen in Equation (10)

$$N_{Nu} = \frac{k_m D_h}{D_{AB}} \quad (10)$$

where  $D_h$  is the hydraulic diameter as defined by Incropera and Dewitt<sup>18</sup>. Incropera and Dewitt also suggest a Nusselt number in laminar flow for given aspect ratios. For an aspect ratio (height of channel to length of channel) of a square channel, the Nusselt number was determined to be 2.98. By application of this to a system in which there is a zero concentration of A at one surface (infinite mass flux at the surface), and an infinite flux through the membrane separating the two sides, we can determine the diffusion limited current density ( $i_d$ ) needed to provide for the transport for given concentrations through Equation (11)

$$i_d = nFk_m \rho_{molar} \Delta x_{lm} \quad (11)$$

where  $n$  is equivalents/mol;  $F$  is Faraday's constant,  $\rho_{molar}$  is the molar density, a function of temperature in the gas phase; and  $\Delta x_{lm}$  is the log-mean mole fraction difference. This diffusional current density represents the best possible removal for a given system geometry at set system parameters. It does not take into account the effects of transport at any other point in the system. While achievement of the diffusional current density is very possible, initial testing of systems, in general, will fail to yield the high fluxes predicted from a diffusion limited transfer.

In addition, the equilibrium potential of the system can be predicted through the Nernst Equation (Equation (12)).

$$E_s = E_o - \frac{RT}{nF} \ln \left( \frac{a_{products}}{a_{reactants}} \right) \quad (12)$$

where  $a$  is the activity of the species involved in the reaction. The activity of gaseous species can be approximated as their partial pressures in atmospheres, and the standard potential can be determined from Equation (13).

$$E_o = \frac{-\Delta G_f}{zF} \quad (13)$$

where  $z$  is charge; in this case equal to +1. The gibbs free energy of formation has already been determined to be -81.904kJ/mol based on Equation (8).  $E_o$  is then 0.849V. Taking these factors into account, Equation (12) at 400° C becomes:

where  $p_i$  is the partial pressure of component  $i$  in atmospheres. For a given system configuration, and known partial pressures, the potential and current required for a

$$E_e = 0.849V - 0.058V \ln \left( \frac{p_{O_2}^{\frac{1}{2}} p_{N_2}^{\frac{1}{2}}}{p_{NO}} \right) \quad (14)$$

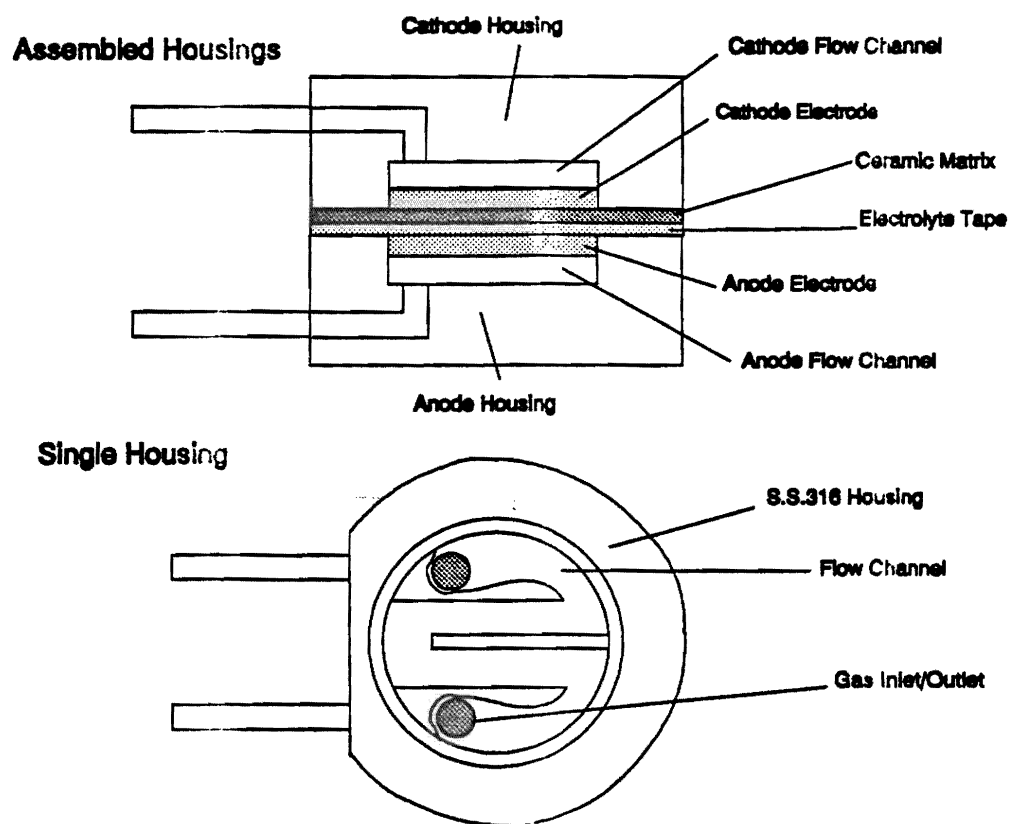
known separation can be calculated. Due to the inefficiency of current in testing up to this point (see Results section), the total cell voltage will be assumed to be 1V under ideal conditions. This voltage should be attainable for an understood system.

## Results

The modeling cell consists of two 316L stainless steel housings with flow channels and electrode supports bored in. These housings are separated by a ceramic matrix, which holds the electrolyte in situ (see Figure 7). Solid electrolyte is incorporated into the cell initially, but melts to flood the ceramic matrix and wet the porous electrodes upon reaching its melting temperature of approximately 325° C.

The electrode used are porous Lithiated NiO. Porous Fibrex Ni sheets have been obtained courtesy National-Standard. Lithiation and oxidation occurs prior to usage in the cell, creating a p-type semiconductor. Conductivity measurements at room temperature yield a resistivity of less than 1Ω, and generally on the order of 0.2 Ω.

The electrolyte is 99.8% pure potassium pyrosulfate ( $K_2S_2O_7$ ) with vanadium pentoxide ( $V_2O_5$ ) in a 90%  $K_2S_2O_7$ /10%  $V_2O_5$  mixture by weight. The exact melting point of this mixture is a function of the bisulfate formation in the pyrosulfate i.e. the extent of contact with water vapor. These bisulfates, while reducing the melting point, will decompose into pyrosulfate upon melting in a predominately pyrosulfate environment.



**Figure 7: Full scale testing housing and geometry.**

## NO<sub>x</sub> Removal by McHenry

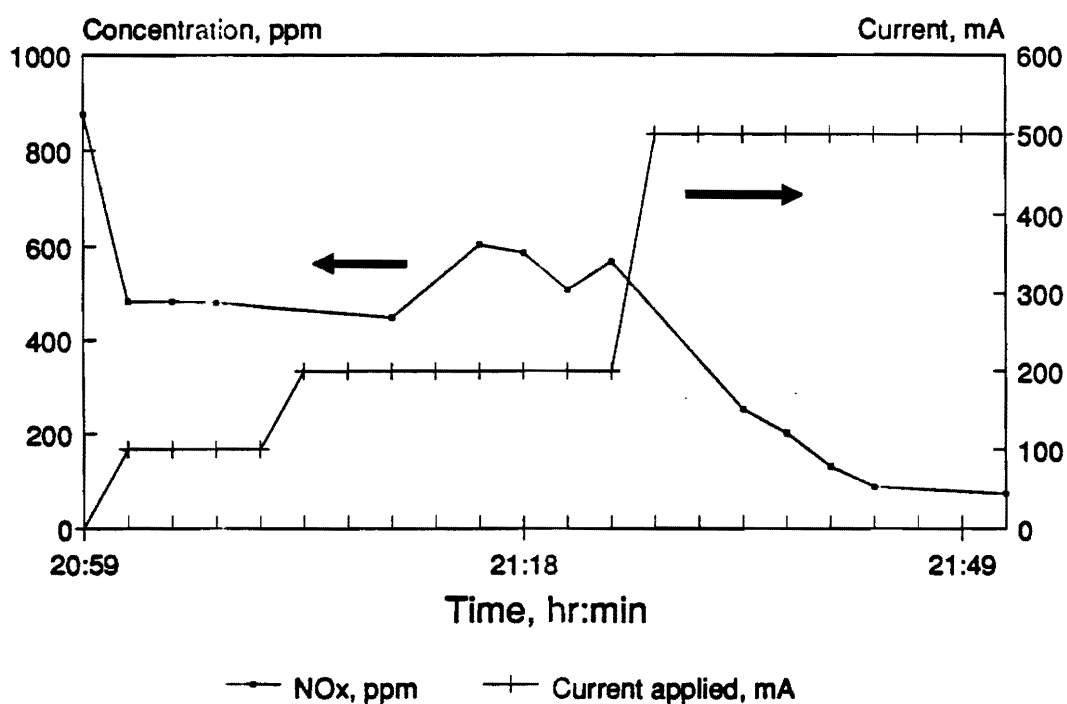


Figure 8: Electrochemical removal of NO<sub>x</sub> from flue gas achieved by D.J. McHenry.



90% removal of  $\text{NO}_x$  from gas streams at  $400^\circ\text{C}$  has been accomplished by McHenry<sup>19</sup> in a full cell test model. The electrolyte used was  $\text{K}_2\text{S}_2\text{O}_7/\text{V}_2\text{O}_5$  in a 90/10 respective weight ratio. Inlet levels of  $\text{NO}_x$  were 850ppm in  $\text{N}_2$ . Removal achieved a level of 75ppm  $\text{NO}_x$  (see Figure 8) with a corresponding current density of  $25\text{mA}/\text{cm}^2$ . The ceramic matrix was made of  $\text{Si}_3\text{N}_4$  particles of  $2\mu\text{m}$  diameter obtained courtesy Phillips Petroleum.

In addition, testing of the removal ability was performed with the use of a  $\text{ZrO}_2$  membrane obtained from Zircar Fibrous Ceramics Company. This removal was attempted with higher flow rates, and yielded excellent removal (see Figure 9). While removal was not as high on a percentage basis, the flux achieved with lower current densities was as good as or better than those achieved by McHenry. Table I shows the fluxes achieved are not as high as those predicted by the diffusion limited current for the system, but show excellent results, nonetheless. The cell test with the  $\text{ZrO}$

## NOx Removal ZrO<sub>2</sub> Membrane

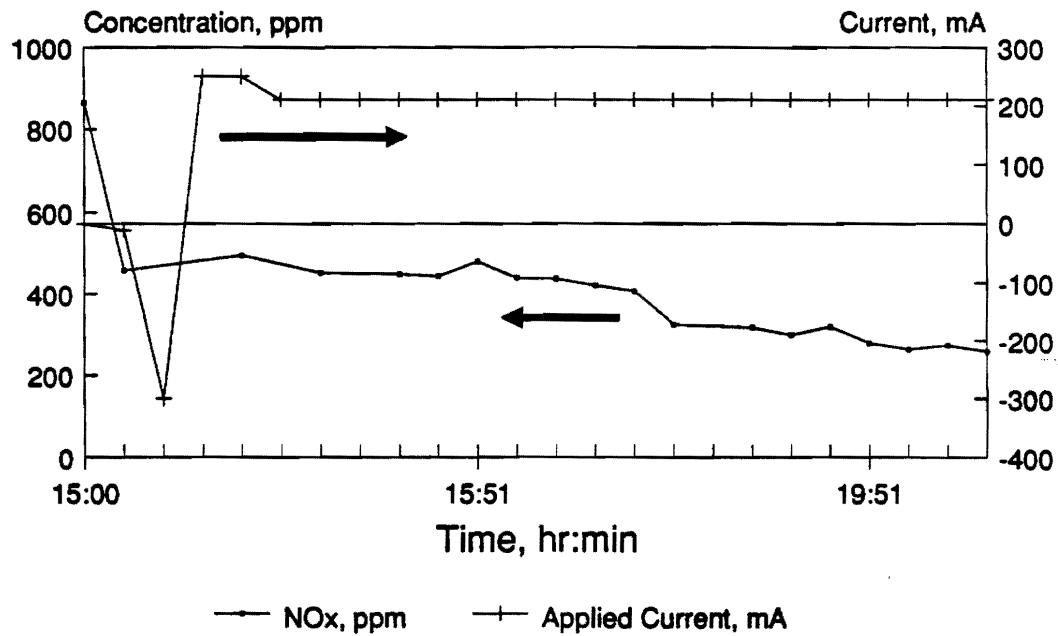


Figure 9: Removal with the use of the ZrO<sub>2</sub> membrane.

<sub>2</sub> membrane in fact achieved an excellent flux. Because this last flux is so close to that of the diffusion limiting case, the diffusion limited current will be used to predict the various aspects of the stack envisioned for the process.

Experimental current efficiency for these experiments was on the order of 10% for a one electron process, where one electron removes one molecule of NO. This low efficiency could indicate a more complex mechanism than proposed (see Theory). It could also be an indication of more electron usage per molecule transferred. The exact number of electrons need for the transfer mechanism has not been determined.

By considering Equation (8), a cause of the less-than-ideal removal of the system may be the fact that the sweep stream that has been used to this point is N<sub>2</sub>. The high pressure of

nitrogen may force the overall reaction in the reverse direction to an extent, requiring higher currents and overpotentials to achieve the desired removal.

Table I: Comparison of achieved and diffusion limited fluxes.

Run Type, membrane	Removal, ppm	Flux, mol/cm <sup>2</sup> /sec	Diffusion limited flux, mol/cm <sup>2</sup> /sec
McHenry, Si <sub>3</sub> N <sub>4</sub> (Case 3)	850 to 568	$2.000 \times 10^{-9}$	$2.551 \times 10^{-7}$
McHenry, Si <sub>3</sub> N <sub>4</sub> (Case 2)	850 to 74	$5.921 \times 10^{-9}$	$1.159 \times 10^{-7}$
Present, ZrO <sub>2</sub> (Case 1)	865 to 308	$6.079 \times 10^{-9}$	$9.834 \times 10^{-9}$

In the same

respect, any  $O_2$  produced in Equation (3) will also decrease the removal at a given current, by, once again, forcing Equation (8) to the left.

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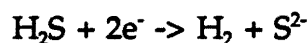
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## II. H<sub>2</sub>S Removal Cell

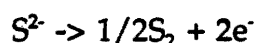
### Introduction

This electrochemical cell purges a fuel gas contaminated with H<sub>2</sub>S.

This is done by reducing the best lewis acid in the gas stream. In this case H<sub>2</sub>S is electronated by the following:



A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the sulfide ions across to the anode. If the membrane is impermeable to H<sub>2</sub> diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur away to be condensed later.



### Research Summary

New experiments are being done using a Zircar Manufactured membrane for removal of H<sub>2</sub>S from a fuel gas stream. The manufactured membrane is advantageous due to the lack of warping and uniform porosity. This allows equal migration of sulfide ions throughout which in turn gives a uniform current density. Both stainless steel and MACOR cell housings have been used with promising results. Although no removal was seen with the stainless steel housings (run #1), the seals lasted strongly throughout, holding back pressures up to 30 mm H<sub>2</sub>O. Over 90% removal with applied current was shown using the MACOR housings, even at high flow rates (200 cc/min - 800 cc/min)(run #5). Another alternative membrane was produced in our laboratory which

was used with the MACOR housings (run #4). Over 90% removal of  $\text{H}_2\text{S}$  with applied current was also recorded with this membrane, but using low flow rates (200 cc/min). All runs operated at  $650^\circ\text{C}$ . Work has continued with an attempt to focus on sealing the housing for more accurate removal data.

## A. Experimental Run Results

### Run #4

A self-produced rigid Zirconia mat worked in this experiment. The mat began as a weave of zirconia cloth, then hardened with the zirconia rigidizer. All other equipment remained the same as runs 2 - 5. The temperature and flow rate were maintained at  $650^\circ\text{C}$  and 215 cc/min respectively. Inlet concentration was held between 6 and 20 ppm  $\text{H}_2\text{S}$ . As much as 94% removal with applied current was seen in this experiment as shown. Exit  $\text{H}_2\text{S}$  and applied current vs potential difference (cathode to anode) are shown in figures 1 & 2. The results of both run 4 & 5 are tabulated in Table 1. The experiment was shut down due to hydrogen cross-over. Run #4 lasted 163 hours.



### Cross-cell Potential vs H2S Removal Run #4

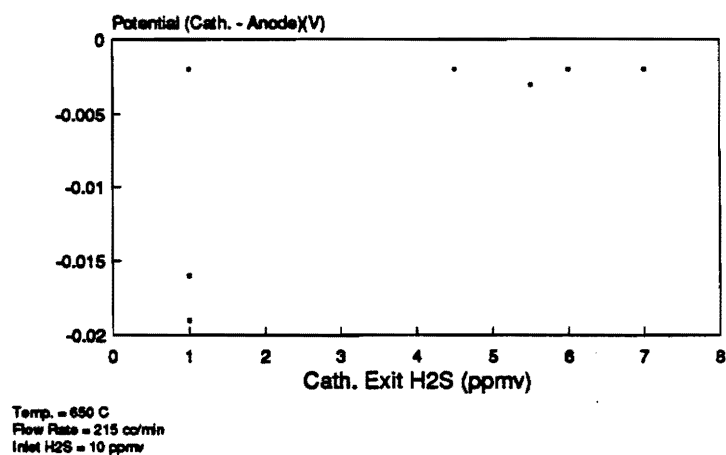
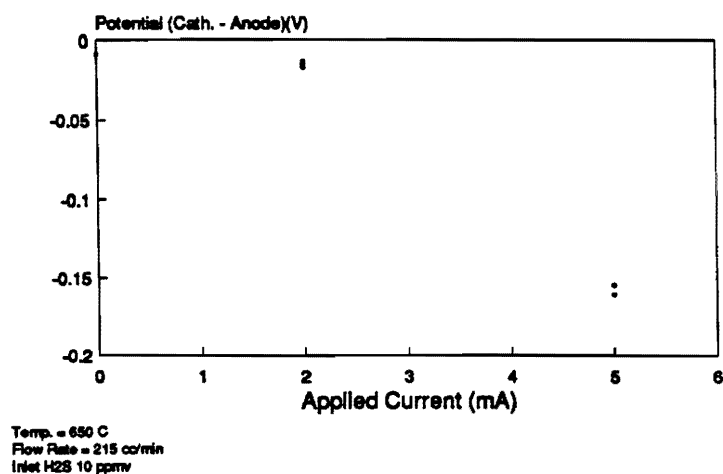


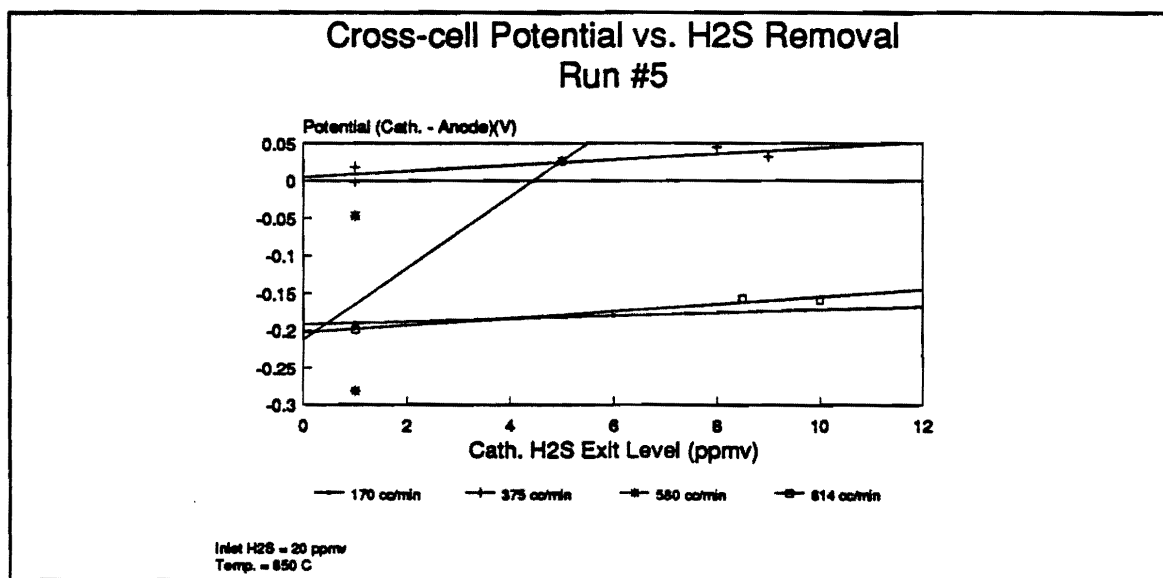
Figure 1

### Cross-cell Potential vs. Applied Current Run #4



Run #5

A manufactured Zircar membrane provided the medium for electrolyte support. The membrane is advantageous, due to uniform porosity (66%) and no warping. The flow rates varied (200 cc/min - 800 cc/min), temperature remaining constant (650° C). Removals over 90% were recorded with applied current. Exit H<sub>2</sub>S and applied current vs cross-cell potential (cathode-anode) are shown in figures 3 & 4. The cell was shut down after 208 hours, due to an increase in membrane thickness, limiting sulfide migration.

**Figure 3**

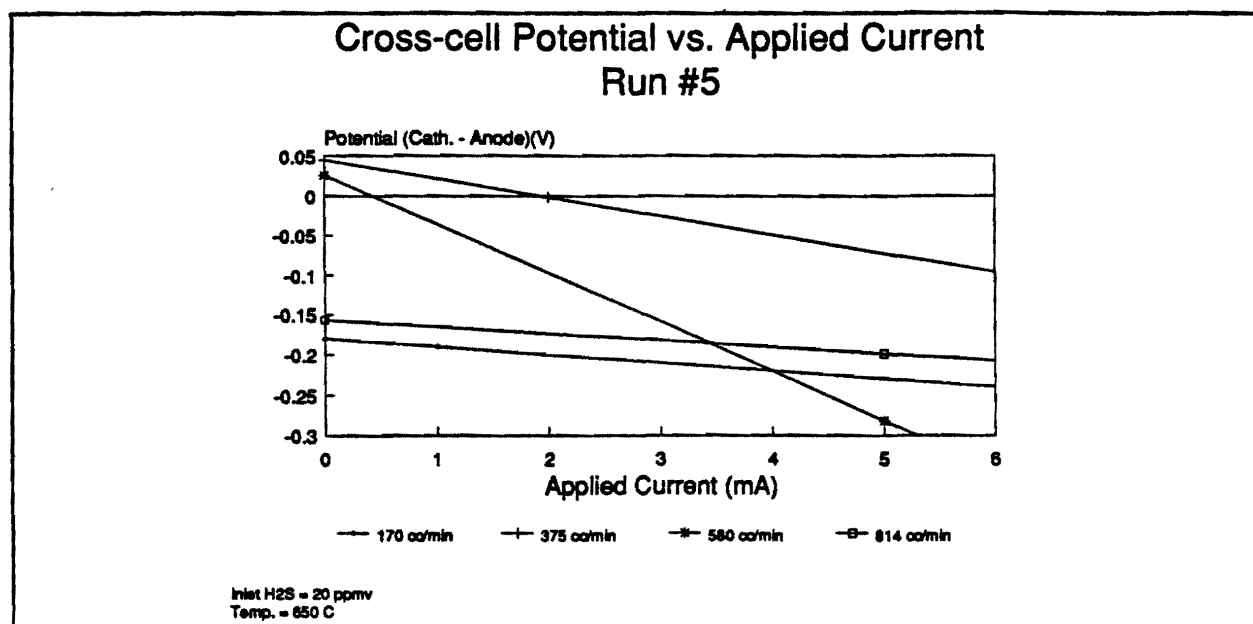
**Figure 4**

Table I. Experimental Results for Runs #4 & #5

<u>Temp.</u> <u>(°C)</u>	<u>Flow-Rate</u> <u>(cc/min)</u>	<u>Residence</u> <u>Time (sec.)</u>	<u>Inlet H<sub>2</sub>S</u> <u>(ppm)</u>	<u>Exit H<sub>2</sub>S</u> <u>(@ I<sub>app</sub>)</u>	<u>I<sub>app</sub></u> <u>(mA)</u>	<u>E<sub>c.a</sub></u> <u>(Volts)</u>
650	170	0.197	25	1	1	-0.190
	225	0.146	8.5	1	2	-0.013
	375	0.089	22	1	2	-0.003
	580	0.058	20	1	5	-0.047
	814	0.041	22	1	5	-0.199

### Run #1

Stainless steel housings were used to test resilience. Seals were formed from painting the housings with Al paint (29% Al). The housings were then baked in an oxygen atmosphere to form alumina, later forming a seal in-situ by reacting with Li in the electrolyte to form  $\text{LiAlO}_2$ . This run was successful in sealing the housings which was shown by holding up under back pressures as high as 30 mm  $\text{H}_2\text{O}$ . No effective removal data was taken from this run, but the experiment lasted for 453 hrs, keeping strong seals throughout.

### Run #2 - #3

These experiments are combined due to the usage of the same type Zircar manufactured membrane for both. Lithiated Ni were used as electrodes and aluminum paint was applied to the MACOR housings for sealant. The electrolyte was a prepressed disk.

Run #2 lasted only 48 hrs due to carbon build up between the cathode electrode and the membrane. This was caused by the bourdouart reaction, avoidable by increased hydration of the fuel gas.

Run #3 lasted only 24 hrs due to the cracking of the membrane and lack of seals. There was no outflow of gas.

### **Summary**

Polishing of 10 ppm hydrogen sulfide to ~1 ppm has been demonstrated this quarter with varying flow rates. Hydrogen cross-over has been slowed but not completely cured, although the Zircar manufactured membranes sustained runs for several weeks. Sealing the cell housings presents the biggest challenge in the upcoming quarter in order to maintain adequate data collection.

#### **Planned work for Next Quarter**

Work will continue with improving seals as well as working with the Zircar manufactured membranes, but producing our own membranes (Run #4) is becoming more important due to economic reasons. Both Stainless steel and MACOR housings will be used in the next quarter.

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**Quarterly Progress Report:**  
**High Temperature Membranes for**  
**H<sub>2</sub>S and SO<sub>2</sub> Separations**  
**Grant DE-FG22-90PC90293**  
**October 1, 1992 - December 31, 1992**

**by**

**Professor Jack Winnick**  
**Georgia Institute of Technology**  
**School of Chemical Engineering**  
**Atlanta, Georgia 30332-0100**



## **Purpose and Goals of Research**

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification,  $\text{H}_2\text{S}$  has been removed from the syn-gas stream, split into hydrogen which enriches the syn-gas, and sulfur which can be condensed from an inert gas sweep stream. For coal combustion,  $\text{SO}_2$  has been separated from the flue gas, with concentrated  $\text{SO}_3$  produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  cells require more efficient membranes and the  $\text{H}_2\text{S}$  cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies, or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress toward these goals.

## I. SO<sub>x</sub> Removal Cell

### INTRODUCTION

Successful removal of SO<sub>x</sub> from flue gas depends on the development of a membrane able to achieve a current density of 50 mA/cm<sup>2</sup> at a total voltage of approximately 1V. Flooding of electrode has been identified as a problem, leading to increasing polarization over time. The resulting reduction of surface area also tends to limit the mass transfer flux, reducing the efficiency of the cell. To reduce flooding, new materials and techniques of manufacture will be investigated, in the attempt to produce a ceramic membrane of approximately 50% theoretical density. This membrane must have proper pore size distribution to ensure sufficient capillary force to prevent impregnated electrolyte from flooding electrodes, and subsequently drying the ceramic membrane. Various methods of matrix production were studied this quarter: tape casting, pressing and sintering, and slip casting. Each will be discussed in turn.

Electrolyte introduction to the cell is a continuing problem. The development of a method is still being investigated. Ideally, the electrolyte would be introduced as powder with binder in a green body. This binder would burn away at temperatures of approximately 300° C, leaving pure electrolyte to melt and complete the ionic path necessary for the electrochemical cell. The electrolyte used this quarter was, exclusively, a 90wt%K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>/10wt%V<sub>2</sub>O<sub>5</sub> mixture.

Electrodes used this quarter were lithiated nickel oxide. These were obtained from National Standard (Fibrex) and the Energy Research Corporation (ERC) as Ni sheets. These sheets were cut, with a resulting superficial area of approximately 20.0cm<sup>2</sup>. The cut Ni was placed in a 1-2M solution of LiOH, dried, and oxidized at 600° C prior to placement in the cell. This process creates a p-type semiconductor, exhibiting room resistivities on the order of 1.0-0.2Ω at room temperatures. Pore size of the National Standard Fibrex electrodes is approximately 1.0 μm. The pore size of the ERC electrode is proprietary. Other methods of manufacture of the electrodes were studied this quarter, and will be detailed as such.

Current is conducted through the cell from stainless steel 316L housings, to the electrolyte-wetted electrode, where the removal takes place. The current is then carried through the cell by the transporting species in the electrolyte. Oxidation of the transporting species occurs at the anode, and the current passes through the anode electrode to the anodic SS316L housing, and out of the cell.

## **MATRIX MANUFACTURE**

Four methods of matrix manufacture were attempted this quarter, with varying success:

- (1) Pressing of VK-38 catalyst with and without electrolyte
- (2) Tape casting
- (3) Slip casting

#### (4) Pressing and Sintering

In addition, a sample of silicon nitride was obtained from the Oak Ridge National Laboratory, courtesy O.O. Omatete, and additional silicon nitride was obtained from Phillips Petroleum, courtesy L. Kallenbach. A sample of boron nitride was obtained from Carborundum, Inc.. The Phillips Petroleum silicon nitride was used exclusively this quarter, but testing of the Oak Ridge silicon nitride and the boron nitride will be pursued this quarter.

##### Pressing of VK-38

VK-38, a sulfuric acid catalyst obtained from Haldor-Topsoe, was crushed to a median particle size by weight of  $90.67\mu\text{m} \pm 11.12\mu\text{m}$ . This powder was then pressed at 4000 psig for 5 minutes in a 3" diameter die. The resulting disk crumbled easily. A second attempt was made, and after pressing, the disk was heated to 350° C before removal from the die. The heat was used in an attempt to allow the pyrosulfate present in the catalyst to melt and form a hard solid. The resulting disk was exceedingly fragile to the touch, and large portions of the disk broke before it could be tested in a full scale cell. This process was abandoned.

##### Tape Casting

Tape casting was attempted with very little success. As has been reported in the past, casting has been successful using the Phillips Petroleum 0.2 $\mu\text{m}$  silicon nitride particles, in only a 30vol% loading level. This low loading level led to the mechanical inability to support any type of structure necessary for use as an electrochemical

membrane. Silicon nitride seemed to be turned into almost a slurry in the molten pyrosulfate, allowing easy gas passage.

The casting procedure used utilizes a polyvinyl butyryl binder, in a benzene/toluene solvent. This prepared mixture, including some dispersants and surfactants, was obtained from Metoramic Sciences. The binder is added in an appropriate quantity, such that, after burnout, the resulting ceramic and ash left will occupy 50% by volume of the apparent volume of the ceramic disk.

After binder mixing, additional solvent and surfactant is added as needed to keep the solution at an appropriate viscosity. No consideration of pH has been applied to this time. The slurry is mixed in an alumina ball mill, and is sonicated prior to casting.

Casting takes place on an appropriate surface, either glass, galvanized steel, or teflon, depending on the surfactant and dispersants used in formulation. Spacers are used so that a doctor blade may be drawn across the surface at a height of 1 mm relative to the surface. The mixture is poured across the surface, and the doctor blade is drawn across to produce a uniform height. The wet tape is then covered completely to slow down the evaporation of the solvent, allowing the tape to dry uniformly, without cracking or undue stress. Drying is done overnight, or as required.

The resulting green tape is then removed from the substrate, and cut to the proper form. It can be pressed, combined with other tapes, and generally used as desired, as it is extremely pliable at this point. As the tape is subjected to higher and higher temperatures, as in full cell tests, the organics volatilize with oxygen, and burn out

completely by 380° C, according to a Metoramic Sciences TGA, leaving only a small amount of ash. The resulting ceramic matrix is then impregnated with electrolyte.

Various problems have arisen in the application of this much-desired process. The attempt to tape-cast such a small particle size, with such a large surface area (80 m<sup>2</sup>/g), is somewhat unprecedented in a 50 vol% loading level. There is a constant problem of surface wetting by the polymer due to the large surface area. The natural alleviation of this problem is the addition of binder to the system. This will result, however, in the reduction of volume percent ceramic, which leads, as previously discussed, to a mechanically intolerable system.

Additional solvent is then the possible solution. The result, however, tends to choose one of two avenues: the large amount of solvent evaporation leads to a cracked green tape; or the mixture is not homogenous, with viscous and less-viscous phases present, resulting in a non-uniform green tape. Neither of these two results is at all desirable.

Additional surfactant has been tried in an attempt to reduce the amount of solvent required to obtain a homogenous mixture. This carries its own problems: solvent evaporation will be slowed down at the surface, as the surfactant increasingly inhibits easy solvent evaporation as it travels to the surface with the solvent and accumulates due to its lower vapor pressure. Again, internal stress may result, as solvent is trapped inside the drying tape, resulting in cracking of the tape.

Solutions to this problem have been discussed with Metoramic Sciences<sup>1</sup>. Among the solutions discussed is the variation of solvents to from just ethanol and toluene to

include possibly acetone or MEK. Some of these may not be feasible, however, as the rate of evaporation would increase in some cases, possibly leading to cracking. Additional surfactants were also been discussed, including acetates, high carbon acids, and possible phosphoric acid, along with some amides, aminos, and polyesters. None of these suggestions has been attempted at this point, but will be should other methods of membrane manufacture prove unacceptable.

### Slip Casting

As a unique method, slip casting of the silicon nitride was attempted. Slip casting, is the mixing of the ceramic into a slurry, and pouring the slurry into a mold. The solvent is drawn off by the mold, leaving the resulting ceramic in the desired shape. Thickness is controlled by the solvent/ceramic ratio, speed of casting, and relative solvent humidity conditions. The casting solution may contain only the solvent, or some mixture of solvent, binder, surfactant, or dispersant, all of which will affect the casting ability and resulting ceramic piece.

The attempt was made, again using the Phillips Petroleum silicon nitride, in conjunction with water as the solvent, and using Darvan C, courtesy Konrad C. Reiger of the R.T. Vanderbilt Company, Inc., as the dispersant, to slip cast a membrane. Darvan C has a low ash content on burnout, and has shown low foaming in Vanderbilt tests.

A slurry was mixed in a beaker, with DI-H<sub>2</sub>O (18.3  $\Omega$ -cm), Darvan C, and silicon nitride in a, respectively, 48.3 wt%/0.3 wt%/51.4 wt% mixture, for a total of 20.570g. Mixture viscosity was visually estimated as correct. The slurry was then poured into the

full cell housings, with electrodes in place, and the top housing was pressed onto the slurry top to form a membrane of a thickness of approximately 1.5mm. Unfortunately, the electrodes and housings were dry, and the water was quickly absorbed into the electrodes, setting the slurry in a less-than-ideal configuration. It was felt, however, that despite the problems encountered, and the resulting thick membrane, the cell could be properly sealed when wet with electrolyte.

The cell never did seal, using an estimated amount of electrolyte, and the cell test was terminated. Upon post-mortem examination, however, the membrane was found to simply be deficient in electrolyte, and wetted only on the top. Had additional electrolyte been added, the cell might have succeeded. Further testing of this method will involve the saturation of the electrodes and housings with water prior to casting of the slip. This will hopefully allow thinner membranes, while still maintaining a high volume percentage ceramic.

### Pressing and Sintering

Dry pressing, and sintering of ceramic membranes also took place this quarter. Dry powder was packed uniformly into a die of 3" diameter, to thicknesses of 1mm to 1.5mm. The die was then taken to a hydraulic press, with a applied pressure of 1132 psig. The resulting disk is then transferred to a firing plate, covered, and placed in an oven with a slow temperature ramping to 1150° C, held at that temperature for a period of time, and slowly brought back down to room temperature.

The first attempt resulted in an amalgamation of alumina and silicon nitride. The silicon nitride disk, after pressing, was fired on an alumina firing plate in an oxygen



atmosphere. Some unidentified liquid phase formed, resulting in warping of the disk, and the general defacing of the alumina firing plate. It was suggested<sup>2</sup> that the firing be done in an inert atmosphere of nitrogen, and on a surface of either silicon nitride or silicon boride. In addition, a solid-phase diagram was prepared, shown in Figure 1, to ensure the material obtained from the process was the material desired.

A reaction-bonded plate of silicon nitride was obtained from Norton Industrial Ceramics. A test disk of 1" diameter was pressed and fired under high purity nitrogen (Holox, 99.97 purity), with excellent results. The plate obtained, however, was not large enough to support a 3" diameter disk.

Discussion with Paul Kohl, Professor, Georgia Institute of Technology, revealed that the chemical vapor deposition (CVD) of pure  $\text{Si}_3\text{N}_4$  onto Si wafers was common technology. Four such wafers were prepared by Martin Ceiler, Chemical Engineering, Georgia Institute of Technology, with  $\sim 9000\text{\AA}$  of silicon nitride deposited onto the surface.

A 3" diameter disk was pressed at a pressure of 1132 psig, and fired under pure nitrogen, following the ramp seen in Figure 2. The resulting disk was found to be of sufficient mechanical strength, although this was not explicitly tested except in handling. It is known that the sintering of pure silicon nitride results in a final porosity of approximately 65% at a temperature of up to 2073 K<sup>3</sup>. The porosity of the sintered membrane is therefore estimated to be approximately 60%, with the sintering process actually incomplete at the low firing temperatures.

# Si-O-N Phase Diagram For Varying Temperatures

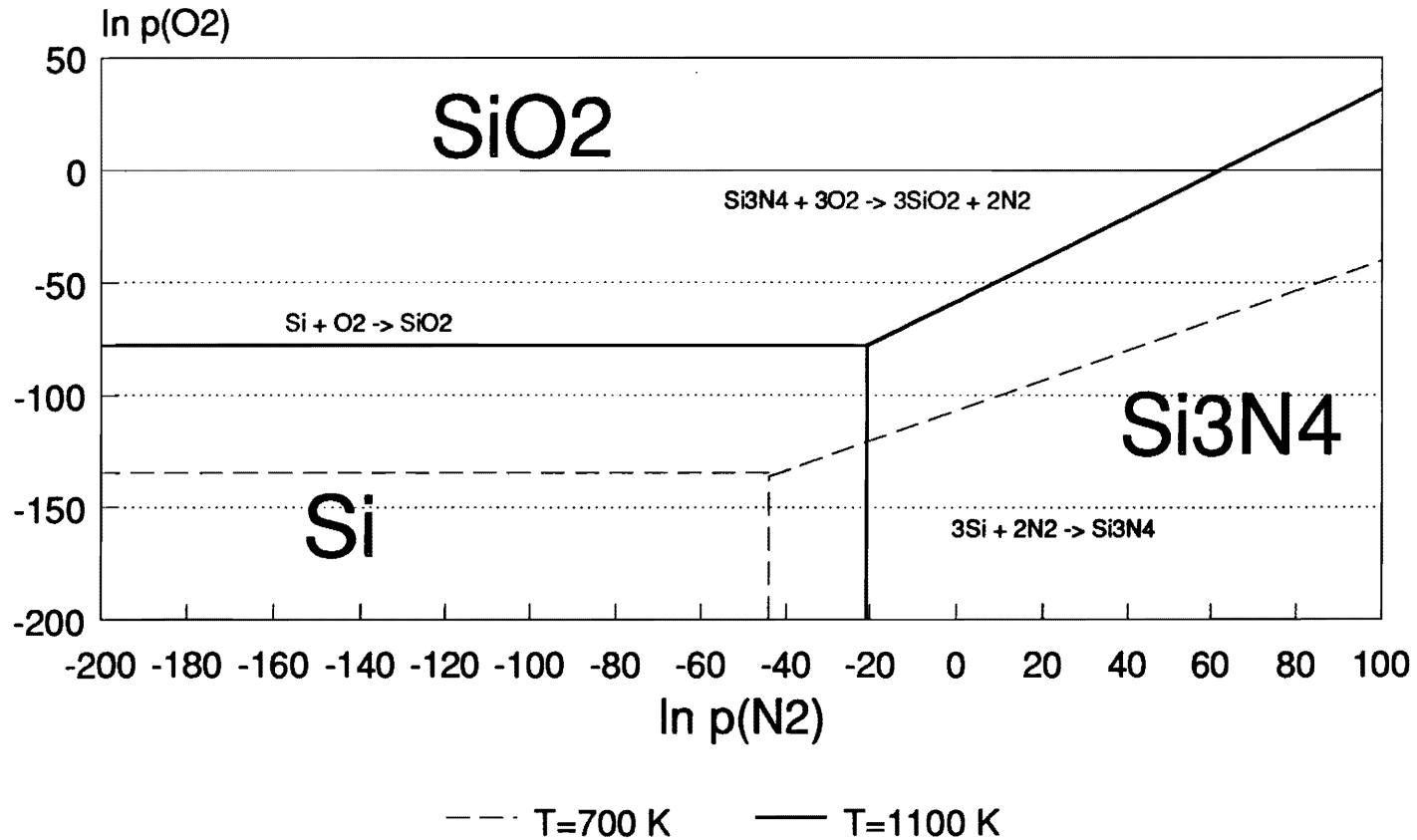
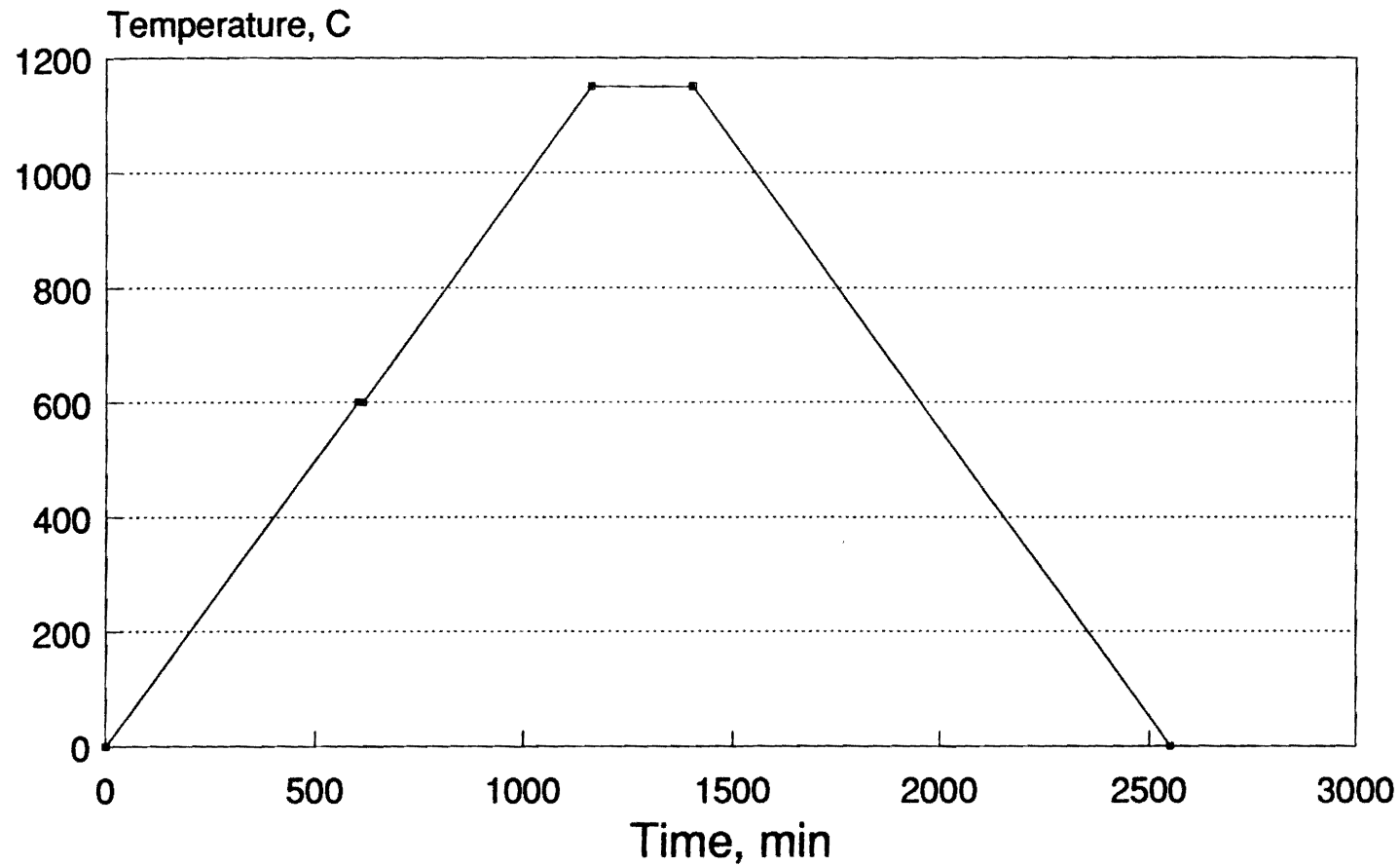


Figure 1: Silicon-oxygen-nitrogen phase diagram for the sintering of silicon at varying temperatures.

The disk was used in a full scale run. Cracking was heard upon cell assembly, but the test proceeded in the hope that the electrodes had broken, leaving the membrane intact. The introduction of electrolyte into the matrix was an unusually slow process, and consequentially, excess electrolyte was added, flooding the electrodes. The concern that, in a time period of 1 hour, the matrix had not been completely wetted was found to unjustified post-mortem, as the small capillaries seem to simply take a longer amount of time to properly wet. The additional electrolyte plugged the outlet tubes. They were immediately cleaned, but gas-crossover began in the interim. The disk, upon examination, was noted to have a few hairline fractures, possibly due to assembly rather than post-mortem examination.

The membrane can be tentatively considered a success. Its wetting capability, now better understood, should be carefully monitored, but the mechanical aspects of the matrix, fabricated in this manner, seem promising.

# Temperature Ramp for Si<sub>3</sub>N<sub>4</sub> Sintering In N<sub>2</sub> Atmosphere



P=1 atm, high purity N<sub>2</sub>

Figure 2: Temperature ramp of the firing of a 3" diameter silicon nitride disk.

## ELECTRODES

The electrodes used this quarter were obtained from ERC. Porosity experiments and measurements were performed with both the ERC electrodes and the Fibrex electrodes, used in previous quarters. The results of the ERC electrodes are proprietary in nature, but the results of the Fibrex electrodes will be reported.

It has been suggested<sup>4</sup> that the electrodes be oxidized, and then lithiated, ex-situ. Presently, the oxidation and lithiation process is a co-current event; the electrodes are soaked in LiOH, and then ramped up to 600° C for simultaneous oxidation and lithiation. They are held at that temperature for a minimum of 8 hours.

Both Fibrex and ERC electrodes were oxidized at 600° C for 8 hours, lithiated in LiOH (saturated), and again placed in air at 600° C for an additional 12 hours. X-ray spectroscopy was performed to confirm lithiated NiO, noted by the slight shift of the peaks due to the incorporation of lithium into the NiO lattice, seen in Figure 3. Porosity experiments were then performed on five samples of each type of electrode, according to ASTM Standard Designation C 373-72. The results of the Fibrex electrodes are shown in Figure 4, along with the formulae used. The electrodes were heated to 150° C for 30 minutes to obtain the dry weight, boiled in water for 5 hours and then let sit overnight to get 25° C water. The saturated specimens were then carefully weighed, according to the standard, to obtain the saturated and suspended weights. These numbers are accurate to at minimum of 2% deviations. Higher accuracies may have been attained.

Sample: LiNiO ERC File: LINIOE.DI

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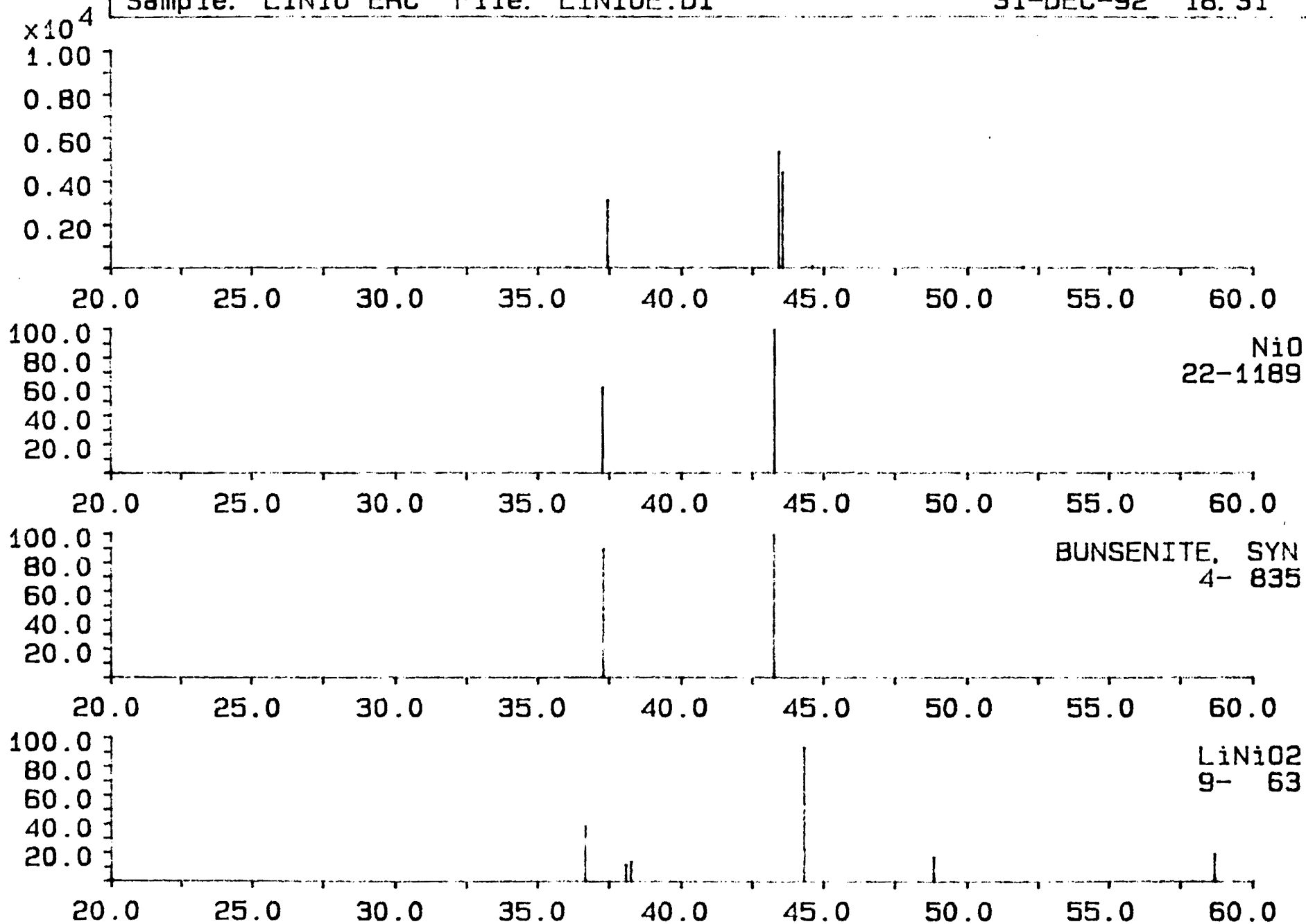


Figure 3: X-ray of oxidized and then lithiated ERC electrode.

**Fibrex Nickel Electrodes**  
**Starting porosity of 86% (Fibrex)**

January 13, 1993	Sample number ->	1	2	3	4	5	Averages	Standard
Measurement	Formula							Deviation
Dry Weight, g	D	1.466	1.674	1.945	1.152	2.045	1.656	0.324
Saturated Weight, g	M	2.644	2.967	3.585	2.159	3.698	3.011	0.577
Suspended Weight, g	S	1.274	1.454	1.661	1.013	1.792	1.439	0.277
		T(water) = 25C density = 1 g/cc						
Exterior Volume, cc	$V = M - S$	1.370	1.513	1.924	1.146	1.906	1.572	0.304
Volume of open pores, cc	$M - D$	1.178	1.293	1.640	1.007	1.653	1.354	0.255
Volume of Impervious Portions, cc	$D - S$	0.192	0.220	0.284	0.139	0.253	0.218	0.050
Apparent Porosity, %	$P = (M - D) / V * 100$	85.99%	85.46%	85.24%	87.87%	86.73%	86.26%	0.96%
Water Absorption, %	$A = (M - D) / D * 100$	80.35%	77.24%	84.32%	87.41%	80.83%	82.03%	3.50%
Apparent Specific Gravity	$T = D / (D - S)$	7.635	7.609	6.849	8.288	8.083	7.693	0.496
Bulk Density, g/cc	$B = D / V$	1.070	1.106	1.011	1.005	1.073	1.053	0.039

**Figure 4: Results of porosity standard on lithiated NiO electrodes (Fibrex).**

Mercury porosimetry was also performed on both Fibrex and ERC lithiated NiO samples, courtesy Westvaco. The pore size distribution in the Fibrex electrode was found to vary widely, primarily from 32.8 $\mu$ m to 0.642 $\mu$ m. The incremental volume per gram can be seen in Figure 5. These values, however, should not be taken literally. Mercury porosimetry has a number of flaws associated with it, including accurate correction for the phase behavior at critical pressures, seen in Figure 6, contact angle determination<sup>5</sup>, rate effects<sup>6</sup>, sample destruction<sup>7</sup>, and the model used<sup>5</sup>.\* Scanning Electron Microscopy is currently being performed on similar samples to determine the relative accuracy of the porosimetry measurements.

Finally, the electrode resistance was measured while the electrode was subjected to temperature cycling. The electrode was attached to gold and platinum leads on either side, and the resistance between these leads measured. Corrections were made for the resistance of the leads, but not for the subsequent oxidation of the alligator clips used. It can be seen in Figure 7 that there is an initial large drop in resistance with increasing temperature. This is believed to be the effect of incomplete lithiation, with completion occurring in the first cycle. The resistance then follows the same curve, but tends to rise slightly. This is believed to be the effect of oxidation of the stainless steel alligator clips used in connection. P-type semiconducting behavior is definitely exhibited, with a resistance of approximately 1  $\Omega$  at 400° C.

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\* A good review of available mercury porosimetry data and limitations can be found in *Powder Technology*, 29(1981), including a bibliography of available literature.



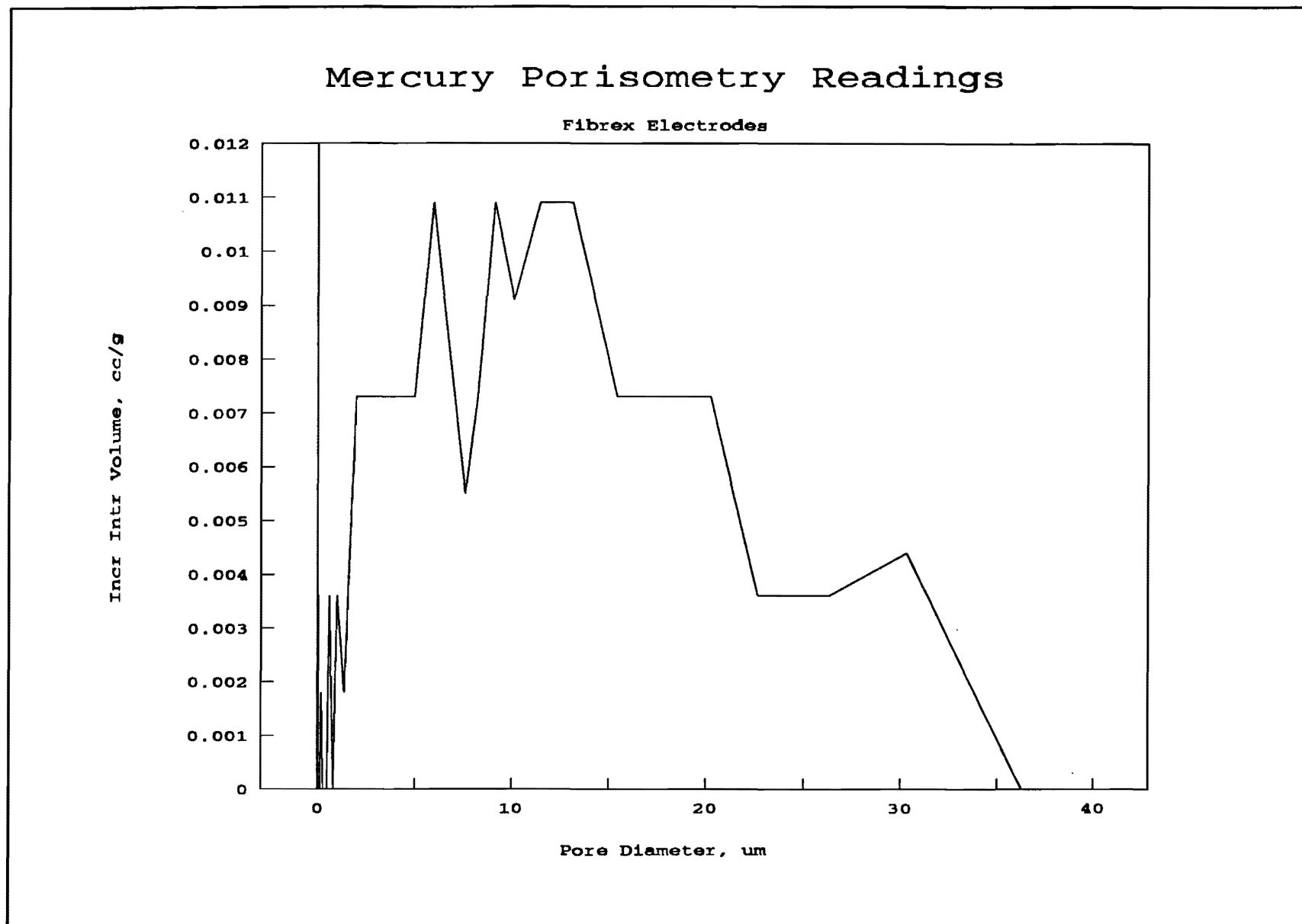
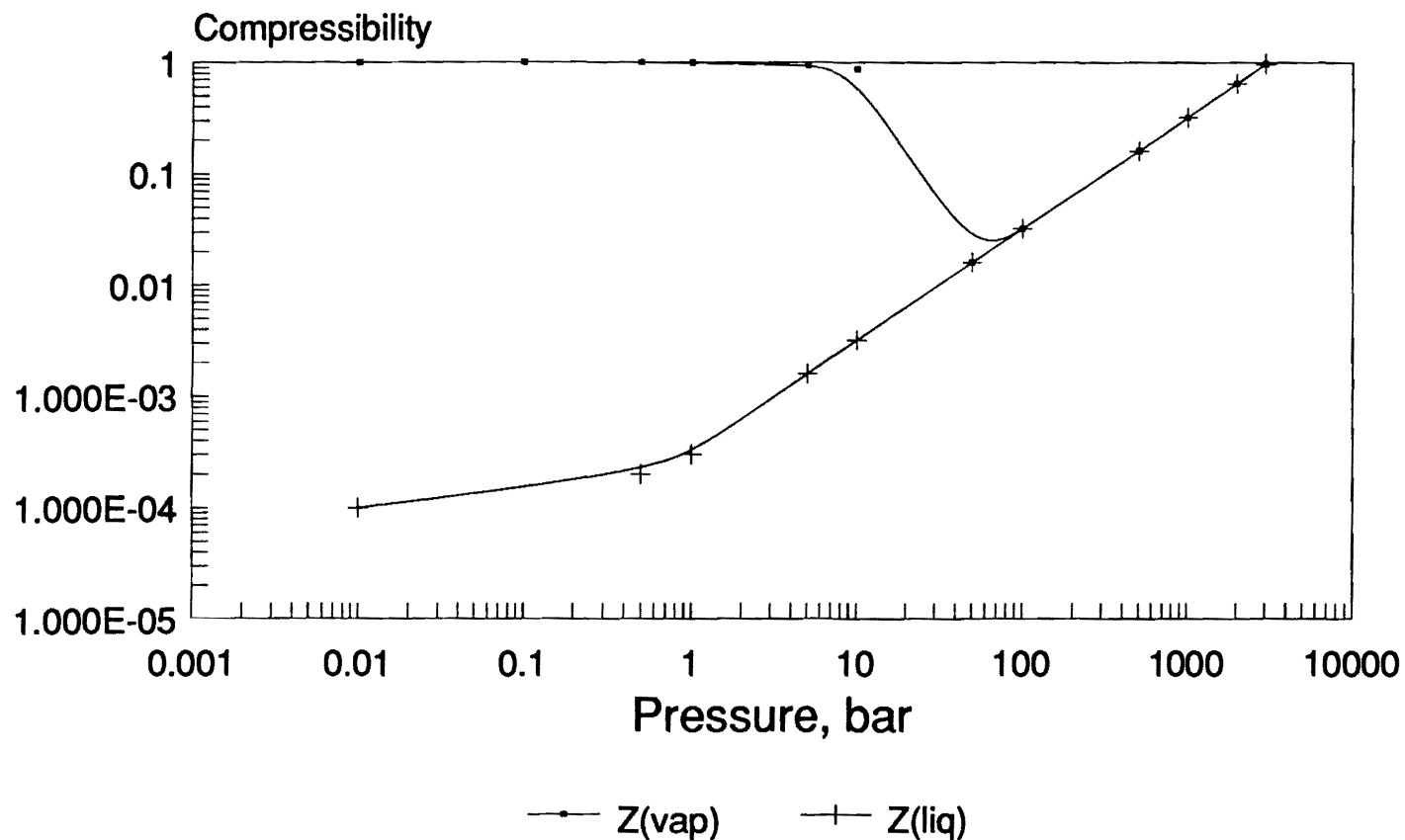


Figure 5: Incremental pore volume obtained from Mercury porosimetry for Fibrex electrodes.

# Phase Behavior of Hg at 298.15K

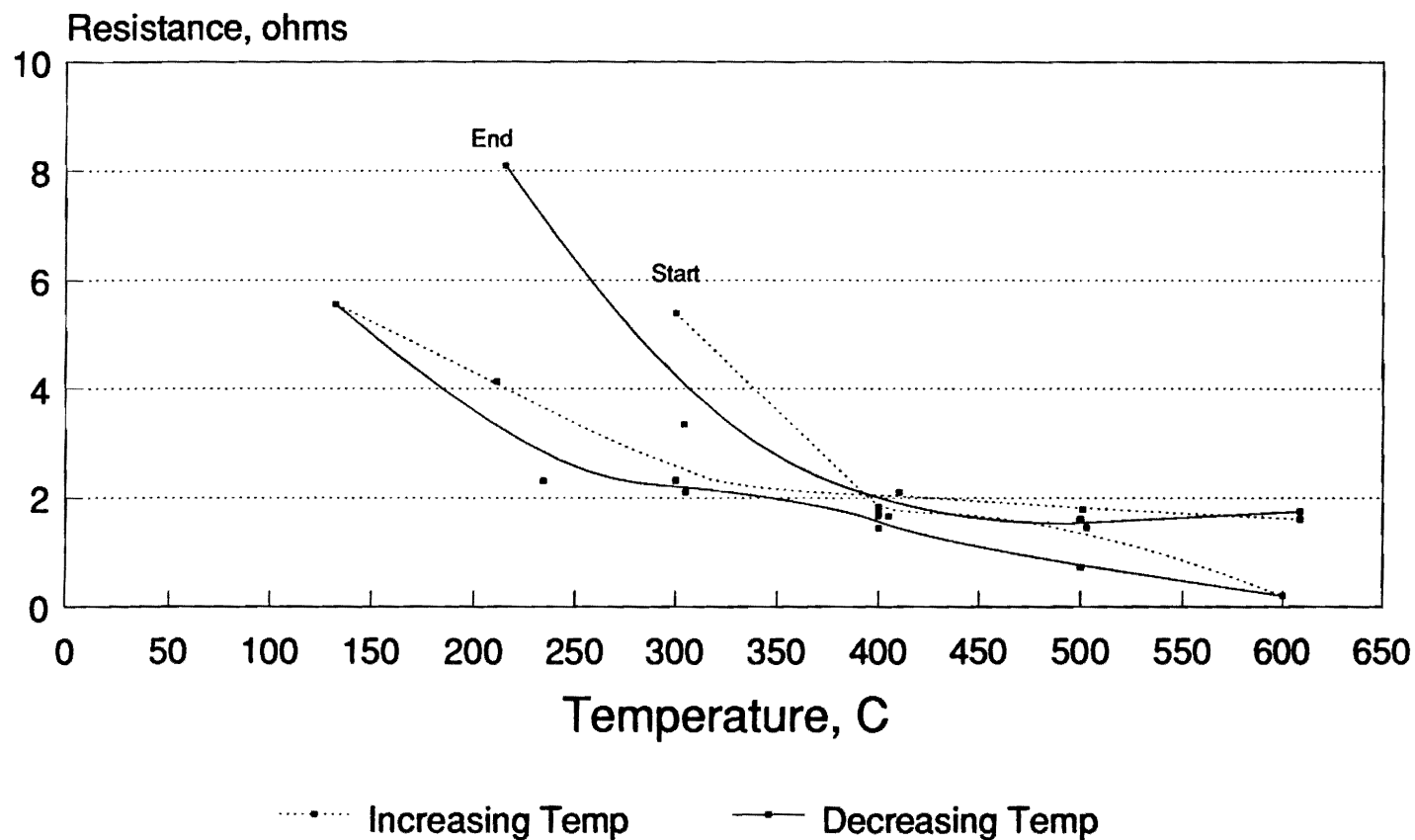


Calculation by Peng-Robinson E.O.S.

Figure 6: Mercury phase behavior with pressures used in mercury porosimetry.

# E.R.C. Electrode Resistance

## p-type semiconductor



1/21+/92, E.R.C.  $\text{Li}_x(\text{NiO})_y$

Figure 7: Cyclic resistance of a p-type semiconductor,  $\text{LiNiO}$ , with temperature.

## FULL SCALE TESTING

There are no definitive results this quarter from full scale tests. The problems encountered with materials have been mentioned. Full scale testing and analysis is currently ongoing with pressed and sintered silicon nitride disks, and initial results do look promising.

## FUTURE WORK

Future work will concentrate on full scale testing, with emphasis on the chemistry involved. Poor long term removal may be due to poor oxygen transport to the vanadium pentoxide catalyst present in the electrolyte. Reduced vanadium ( $V_2O_4$ ) may be the cause for the  $SO_2$  generation noticed at higher currents and flow rates.

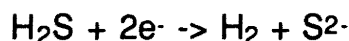
## ENDNOTES

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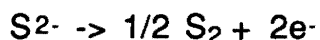
## II. H<sub>2</sub>S Removal Cell

### Introduction

This electrochemical cell purges a fuel gas contaminated with H<sub>2</sub>S. This is done by reducing the best Lewis acid in the gas stream. In this case, H<sub>2</sub>S is electronated by the following:



A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the ions across to the anode. If the membrane is impermeable to H<sub>2</sub> diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur downstream to be condensed.



### Research Summary

Experiments this quarter dealt with application of an electrolyte filled tile. During start-up the electrolyte filled tile relieves the process of pre-pressing an electrolyte disk and in-situ electrolyte infiltration. Also the appropriate amount of electrolyte needed to saturate the tile should already be present, making the tile mechanically favorable. Therefore, alleviating the concern of over or under addition of electrolyte for the tile. If too much electrolyte is introduced to the membrane, flooding of the electrolyte occurs, causing inadequate pore area for electronation of H<sub>2</sub>S. Also, clogging of the flow tubes has been evidenced due to superfluous addition of electrolyte. Under addition, on the other hand reduces the flow path needed to transport the sulfide ions across the membrane. A laboratory replicated membrane along with a Zircar manufactured membrane were also used in other experiments.

MACOR housings were used for runs #6-#9, while stainless steel materials were used in run #10. Electrodes consisted of Ni which transformed to NiO in-situ.

Replication of past experiments which selectively removed 100 ppm inlet H<sub>2</sub>S concentrations, below 10 ppm, were attempted. The start-up problems negated the application of H<sub>2</sub>S to all but run #10. H<sub>2</sub> cross-over prevented any removal data from being collected due to the initial problem of cross-over. This was attributed to lack of stability in the

membranes structure.

In the electrolyte filled tiles the instability of the membranes at molten conditions failed to prevent H<sub>2</sub> cross-over. The high porosity of the replicated membrane also allowed for gas cross-over. The Zircar membrane, however, did provide adequate defense against H<sub>2</sub> crossover. Discussion of individual runs are in the following paragraphs.

#### **Run #6**

This experimental run used a rigidized, electrolyte filled membrane, which becomes molten around 550 °C. Seal development was attempted using aluminum foil gaskets, coupled with an electrolyte-water solution. Seals never developed, but the major problem of hydrogen cross-over caused the shut-down of the run after 166 hours. This cross-over originated because of the lack of structural support once the membrane became molten. Once the cracks developed salvaging the cell became impossible.

#### **Run #7**

Thermal stress caused by thermocouple damage resulted in immediate cracks in the electrolyte filled tile. Shut-down proceeded after 15 hours.

#### **Run #8**

Aluminum paint cooked in an oxygen environment provided the seals in this experiment. The seals never formed to proposed expectation due to the lack of bonding with the MACOR material. The electrolyte filled tile once again weakened under molten conditions, causing cracks in the membrane. Cross-over due to these cracks, progressively worsened the cells performance. Shut-down occurred 24 hours after start-up.

#### **Run #9**

A replication of the Zircar manufactured membranes was produced for this experiment. The optimum porosity should be comparable to that of the manufactured membrane, 66%. Previous successful replicated membranes were 65% porous. An attempt to use an 80% porous membrane in this experiment failed due to a lack of structural support, similar to that of the electrolyte filled tiles. Cross-over resulted, causing shut-down after 24 hours.

**Run #10**

A Zircar manufactured membrane provided the support mechanism for the electrolyte. Seals were developed by initially cooking the housing after coating with aluminum paint. A layer of alumina formed which made available the reaction forming, lithium aluminate, on contact with the electrolyte. Seals developed immediately, but a miscalculation in the amount of water needed for the water-gas shift caused carbon formation in the inlet flow tubing. Once the problem was cured,  $H_2S$  was sent to the cell. Sulfide equilibrium never occurred due to a consistent lack of electrolyte. Continuous addition of electrolyte should have caused flooding of the electrodes, but reaction with the aluminum paint exceeded the small estimates of required electrolyte. Shut-down occurred after 140 hours.

**Summary**

Use of the electrolyte filled tile was inadequate for our research. The instability of the tile, resulting in  $H_2$  cross-over prevented the removal of  $H_2S$ . The Zircar manufactured membrane performed well in the molten environment as expected and will continue to be a focal point of our research. Replication of the Zircar membranes is effective if the porosities are around 65%. The 80% porous membrane produced for in run #9, lacked the stability of a more dense membrane.  $H_2$  cross-over must be stopped to selectively remove  $H_2S$ .

**Planned Work for Next Quarter**

The Zircar membranes will be the focus of next quarters experiments. Replication of these membranes will also continue. If the porosities are controlled the stability of the membrane should follow. Work with sealing the MACOR housings will also continue using aluminum paint.